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Sampling/Analytical Method Evaluation for Ethylene Oxide Emission and Control Unit Efficiency Determinations

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FINAL REPORT

SAMPLING/ANALYTICAL METHOD EVALUATION FOR ETHYLENE OXIDE EMISSION AND CONTROL UNIT EFFICIENCY DETERMINATIONS

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ABSTRACT

Radian Corporation, assisting the Environmental Monitoring Systems Laboratory, Environmental Protection Agency, Research Triangle Park, North Carolina, performed a field evaluation of a method for sampling and analyzing ethylene oxide (EO) in the vent stream from a sterilization chamber and a dilute acid scrubber. The utility of the sampling method for measuring the efficiency of the control unit was also evaluated.

The evaluated sampling and analysis procedure used semi-continuous direct sampling with on-line gas chromatographic analysis. Laboratory studies of the sampling method previous to the field test showed that semi-continuous direct sampling was capable of measuring EO emissions to within 11% of the expected value with a between-trial precision of 5 percent.

Analysis of samples taken from the vent of a dilute acid hydrolytic scrubber indicated that a column that retained dichlorodifluoromethane (CFC-12) longer than EO would be desirable because low part per million by volume levels of EO were difficult to detect in the presence of percent levels of CFC-12. Studies of several types of columns indicated that a stainless steel 10 foot (3 meter) by 1/8 inch (3 millimeter) outer diameter, 5% Flurocol on 60/80 mesh Carbopack B column, provided the best conditions for separation of EO from CFC-12.

Additional studies performed showed that under the field test conditions used, adequate control unit efficiency measurements were obtained using chambers filled with product and assuming that all of the EO charged to the chamber entered the control unit. The field test conditions used included a sterilization chamber/control unit system that was a closed system (i.e. leak-free), and a control unit that had a normal operating efficiency >99.6 percent.

This report contains conclusions and recommendations based on the field test results; descriptions of the properties of EO, the sterilization industry, previously used sterilizer test methods, and the semi-continuous

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direct sampling method; results of the laboratory and field evaluation of the method as well as results of related laboratory studies which were performed; and references used to prepare this report.

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SAMPLING/ANALYTICAL METHOD EVALUATION FOR ETHYLENE OXIDE EMISSION AND CONTROL UNIT EFFICIENCY DETERMINATIONS

SECTION 1

INTRODUCTION

The Source Branch of the Environmental Protection Agency's (EPA) Environmental Monitoring Systems Laboratory (EMSL) at Research Triangle Park, North Carolina, has a program to develop stationary source test methods of known precision and accuracy for use in determining compliance with EPA standards. While participating in this program, Radian Corporation performed a field evaluation of a method for sampling and analyzing ethylene oxide (EO) in the vent stream from a chamber and a dilute acid scrubber of a commercial sterilizer. The usefulness of the sampling and analytical method for measuring the efficiency of the control unit was also evaluated.

Because EPA has listed EO as a possible hazardous air pollutant, a standardized sampling and analytical method is needed for determining control equipment efficiency. The evaluated sampling and analysis procedure used semi-continuous direct sampling with on-line gas chromatographic analysis.

The semi-continuous direct sampling method with on-line gas chromatographic analysis was tested because this method should provide accurate emissions data regardless of the EO concentration profile of the exhaust stream. The sampling/analytical method was tested at the inlet and outlet of the control unit. At the inlet the EO concentration was in the percent range and the temperature was above ambient (120-140°F, 49-60°C) while EO concentrations were in the ppmv range and at ambient temperatures at the outlet.

The measurement of the emissions were used to calculate the EO control unit efficiency. Two calculational methods were evaluated. The first method calculated a through-put efficiency using the EO emissions measured at the inlet and outlet of the control unit. This method calculated a true-efficiency because the EO actually entering the control unit was used in the efficiency calculation. However, there was a greater possibility of error because of the necessity of accurately measuring the inlet flow rate, which entered into the calculation. Measuring the inlet flow rate was complicated by the high EO concentrations and the low flow rates at the inlet.

Measurement of the inlet flow rate was not required using the second calculational method which calculated a recovery that was equated to the control unit efficiency. The recovery was calculated from the amount (weight) of EO charged into the chamber and the measured EO emissions at the outlet of the control unit.

The purposes of the field evaluation were:

- To field test the proposed sampling method on an operating sterilizer with a dilute acid scrubber;
- To evaluate the suitability of the proposed sampling method for determining EO emissions and control unit efficiency; and
- To evaluate the applicability of the measured EO recovery as an estimator of control unit efficiency.

Section 2 reports the conclusions and recommendations based on the test results. Section 3.0 describes the properties of EO and provides a basic description of the sterilization process, the sterilization industry, and previously used test methods. Section 4 describes the method tested. Section 5 contains the results of laboratory evaluations of the method and related laboratory studies. Section 6 contains field test results. Section 7 lists references.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Six conclusions were based on the field test results. First, the sampling/analytical method adequately determined EO emissions at the outlet of the uncontrolled sterilizer (i.e. the EO mass flow rate into the control unit).

Second, the sampling/analytical method adequately determined EO emissions at the outlet of the dilute acid scrubber, but identification of the EO peak in the chromatogram was complicated by EO retention times that shifted as the EO concentration decreased. The EO retention time shift was magnified due to the large range in the EO concentrations. The bias in the sampling/analytical method averaged 7.4% for EO and -2.4% for CFC-12. .

Third, the sampling/analytical method adequately determined the efficiency of the dilute acid scrubber. Measured efficiency calculated by the throughput method for empty chamber tests ranged from 99.82 to 99.98% and averaged 99.94 percent.

Fourth, the recovery method of determining control unit efficiency was comparable to the throughput method at this site. Efficiencies calculated for empty chamber tests by the throughput method ranged from 99.82 to 99.98% and averaged 99.94 percent. Efficiencies calculated for empty chamber tests by the recovery method ranged from 99.90 to 99.97% and averaged 99.95 percent. A one-way analysis of variance (ANOVA) performed on the data for the empty chamber tests showed that the methods were not different. The sterilizer chamber/control unit tested was a closed system (i.e. leak-free) so this conclusion may not be valid at an older facility where more EO may be lost from the system as fugitive emissions.

Fifth, the presence of product in the chamber did not affect the scrubber efficiency measurement. The efficiencies calculated for empty chamber tests by the throughput method ranged from 99.82 to 99.98% and averaged 99.94 percent. The efficiencies calculated for full chamber tests by the throughput method ranged from 99.92 to 99.98% and averaged 99.96 percent.

Sixth, EO emissions and control unit efficiencies calculated using flow rates based on orifice plate data did not differ significantly for EO emissions and control unit efficiencies calculated using estimates based on chamber temperatures and pressures. Ethylene oxide emissions for empty chamber tests based on orifice plate data ranged from 0.011 to 0.043 lb and averaged 0.024 lb. Estimated EO emissions for the same tests ranged from 0.006 to 0.036 lb and averaged 0.017 lb. Throughput efficiencies based on the orifice plate data ranged from 99.82 to 99.98% and averaged 99.93 percent. Throughput efficiencies based on estimated flows for the same tests ranged from 99.85 to 99.99% and averaged 99.95 percent. Again, the sterilizer chamber/control unit tested was a closed system so this conclusion may not be valid at an older facility where more EO may be lost from the system as fugitive emissions.

RECOMMENDATIONS

Six modifications based on the field test results are recommended. These include:

1. For efficiency determinations, sampling at the control unit inlet should not be required when the sterilizer chamber/control unit is a closed system. Sampling at this location is unnecessary because efficiencies calculated by the Recovery Method were comparable to efficiencies calculated by the Throughput Method. The Recovery Method used initial chamber charge and total EO emissions from the control unit outlet to calculate the efficiency.

2. For on-line analysis on a system using EO/CFC-12 sterilant gas, the analysis at the outlet should be modified by using two separate channels, one to quantitate the EO and the other to quantitate the CFC-12. Quantitation of the CFC-12 is needed to calculate the molecular weight of the vent stream. Separate analyses would eliminate the need to program the detector range and the added difficulties produced by detector range programming.

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3. A minimum of six samples should be taken during each evacuation: two during the first two minutes, two between the second and ninth minute, and two between the tenth minute and the end of the evacuation. During the first two minutes of the evacuation the EO and CFC-12 concentrations should be the same as they were at the end of the previous exhaust and should be fairly constant. During the next five to seven minutes the EO and CFC-12 concentrations should change rapidly as the old chamber gas is swept out of the stack and the remaining chamber gas is diluted by the new chamber gas entering the scrubber. After 10 minutes the EO and CFC-12 concentrations should remain fairly constant at a level lower than the initial level.

4. The use of orifice plates should not be required when testing a closed chamber/control unit equipped with chamber temperature and pressure monitors. Field test data showed that the efficiencies calculated using estimated flow data were similar to efficiencies calculated using flow data based on orifice plate measurements.

5. If possible, sampling should be performed offline. Offline sampling would allow more samples to be collected because the number of samples would not be limited by the analysis time. Offline sampling would allow greater flexibility in the analytical method and improve the reliability of the identification and quantification of the components.

6. For offline sampling, 15-second grab samples should be acquired at one-minute intervals during the first two evacuations when the EO concentration is changing rapidly with time. Grab sampling should be performed during the later evacuations at two- or three-minute intervals. Grab samples could be obtained in syringes equipped with valves, small Tedlar bags or Vacusampler® cans.

SECTION 3

BACKGROUND

PROPERTIES OF ETHYLENE OXIDE

The chemical and physical properties of EO are discussed in References 1, 2 and 3. Only a brief summary is included here. Ethylene oxide, an epoxide, is also called oxirane (the International Union of Pure and Applied Chemistry name).[1] Other synonyms include: dihydrooxirene, dimethylene oxide, 1,2-epoxylethane, oxacyclopropane, oxane, oxidoethane, and α,β-oxidoethane.[1] It is usually handled as a liquid under pressure. At room temperature and pressure, EO is a gas that has a pungent, irritating, ether-like odor.[1] At 10 degrees Celsius (^{o}C) [50 degrees Fahrenheit (^{o}F)] it condenses to a colorless liquid.[1,2,3] It is completely miscible with water and with organic solvents.[1,2] The reactive and volatile properties of EO make it highly flammable and potentially explosive.[1,2] It has a flash point of <-18^{o}C (0.4^{o}F) and is flammable in air at concentrations ranging from 3 to 100 volume percent (% [v]).[1,2] It is currently regulated by the Occupational Safety and Health Administration (OSHA) for occupational exposure of 1 part per million (ppm) over 8 hours (hr).[4] Because EO is a known reproductive hazard[2,5] and a suspected carcinogen[5], these last considerations, coupled with the fact that there is no upper explosive limit, require that special safety precautions be taken when handling and storing EO.

GENERALIZED DESCRIPTION OF THE BULK STERILIZATION PROCESS

Detailed descriptions of the sterilization process are contained in References 1 and 6. The bulk sterilization process, used by the majority of the commercial sterilization industry is described here in general terms. Hospital and medical products to be sterilized are preconditioned with steam in a separate chamber prior to sterilization. An air-tight sterilization chamber is loaded with the preconditioned products. Air inside the chamber is evacuated using steam ejectors to decrease the chamber pressure. Once the desired vacuum level is achieved, the air inside the chamber is humidified to a predetermined value by adding steam. The sterilant is pressurized into the chamber to a predetermined level. The chamber is held at a constant pressure for a specified period, during which the products are sterilized by EO. When sterilization is complete, the sterilizer gas mixture is exhausted from the chamber until the chamber pressure is decreased to a predetermined level. Filtered air is introduced into the chamber to flush the sterilant gases from the chamber and product. These air washes may be repeated several times. After the last air wash, the door is opened and the chamber unloaded.

The gas in an EO sterilization chamber does not vent at a constant rate for two reasons. First the initial maximum venting rate is determined by the size of the chamber vacuum pump. As the chamber empties, the vent gas flow rate decreases. Second, the evacuation of the chamber is controlled by a solenoid valve which cuts on and off at regular intervals to prevent the chamber from evacuating too rapidly and damaging the products. This changing and pulsing flow rate makes sampling the gas stream more difficult for two reasons. First, calculating the total flow through the vent is an integration rather than a multiplication process and requires continuous monitoring of the flow. Second, calculating the total emissions requires taking many grab samples over the sampling period or collecting a representative sample using special techniques.

There are two models for the EO concentration profile in the chamber exhaust. In one model the chamber is considered to be a closed system at equilibrium. For this model, the EO concentration in the exhaust gas remains constant and only the vent stream flow rate varies. In the other model, the chamber is considered to be a dynamic system. For this model, both the EO concentration and flow rate of the exhaust gas change with time. If the sterilization chamber does not contain product, the exhaust stream will be characterized best by the first (static) model because equilibrium will occur quickly between evacuations. Any product present in the chamber will offgas, releasing ethylene oxide, during chamber evacuations and air washes. With a product-containing chamber, the exhaust stream will be characterized best by the second (dynamic) model.

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HOSPITAL SUPPLY STERILIZATION INDUSTRY

Throughout the United States and Puerto Rico approximately two hundred facilities use EO for sterilizing heat- or moisture-sensitive products or for fumigating microorganisms and insects.[6,7] Chambers range in volume from less than 2 cubic meters (m^3) [60 cubic feet (ft^3)] to 170 m^3 (6000 ft^3).[7] Throughout the industry 76% of the chambers are charged with a mixture of 12 weight percent (% [w]) EO and 88% (w) of dichlorodifluoromethane (CFC-12).[7] Pure EO is used in 68% of the chambers and mixtures of carbon dioxide and EO are used in 10%.[7] (Some chambers are used with more than one type of sterilant gas.)

The vent streams from 17% of the EO sterilization facilities have some type of control unit, ranging from a neutral-water scrubber to an incinerator.[7] Forty-four percent of the control units chemically hydrolize the EO to ethylene glycol using dilute acid solutions, 3% use catalytic oxidation to convert the EO to carbon dioxide and water, and 19% of the control units are condensation/reclamation systems.[7] Commercial vendors of EO control units include Chemrox Incorporated, Damas Corporation, Mine Safety Appliances (MSA), and Croll Reynolds. A significant segment of the industry has custom-designed control units. Control units have been tested by the manufacturers and the industry as described below. Ethylene oxide removal efficiencies greater than 99% have been measured.[8,9,10,11]

EO CONTROL UNIT EFFICIENCY MEASUREMENTS

Several methods are currently being used in the EO sterilization industry to measure the efficiency of EO control units.[8,9,10,11] In general, the efficiency of an EO control unit is determined on a weight basis over the entire post-sterilization cycle. The post-sterilization cycle includes the initial chamber evacuation and all subsequent air washes. The units tested and reported include:

- A Chemrox unit in Pennsylvania,[12]
- A Chemrox unit in New York,[10]
- A Damas unit,[9] and
- An MSA unit.[13]

The Chemrox unit in Pennsylvania was tested using EO recovery to estimate control unit efficiency. The empty sterilization chamber was charged with a known amount of the EO/CFC-12 sterilant gas and then vented. Grab samples of the vent gas were taken in Vacusampler® cans every 5 min and analyzed in the laboratory. After the air wash portion of the sterilization cycle was completed, an air sample was removed from the chamber. The EO input to the control unit was calculated from the difference of the amount charged to the chamber initially and the amount remaining in the chamber at the completion of the evacuation cycle. The amount of EO emitted from the control unit was calculated from the concentration of EO in the outlet grab samples, the exhaust temperature, and outlet flow rate of the vent gas.

The Chemrox unit in New York was tested using a method whereby direct semi-continuous sampling was performed at both the inlet and outlet of the control unit. Samples were directed through heat-traced lines into the gas sampling valve of a gas chromatograph (GC) at 1 min intervals. The weights of EO at the inlet and outlet of the control unit were calculated from the concentration of EO measured by the GC and the measured temperature and flow rate of the vent gas.

The Damas unit was also tested by taking inlet and outlet samples. The inlet samples were collected in six-layered aluminized bags and the outlet samples were collected on charcoal tubes. A series of inlet and outlet samples were collected at a constant sampling rate over 5 min intervals during the entire post-evacuation cycle. The charcoal tubes were desorbed using carbon disulfide. The bag samples from the inlet and the charcoal tube extracts from the outlet were then analyzed by GC. Again, the weights of EO at the inlet and outlet of the control unit were calculated from the measured EO concentrations, vent gas temperature, and vent gas flow rate during each sampling period.

The MSA unit was also tested using both inlet and outlet measurements. The samples were collected in 10 milliliter (mL) syringes at 1 min intervals. Stream flow rates and temperatures were recorded at the time of sample collection. The entire sample in the syringe was injected directly onto a GC column for analysis. The amounts of EO at the inlet and outlet of the control system were calculated from the measured EO concentrations and stream flow rates.

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SECTION 4

SEMI-CONTINUOUS DIRECT SAMPLING AND ANALYTICAL METHOD DESCRIPTION

APPLICABILITY AND PRINCIPLE

Applicability

This method applies to the measurement of EO emissions from sterilization chambers. It is applicable to emissions from sterilization chambers and sterilization control units which use acid hydrolysis to remove the EO. The analytical method is capable of measuring from 0.03 parts per million by volume (ppmv) to 27.7% (v).[14]

Principle

Samples are collected from the sterilization chamber or control unit using a semi-continuous direct sampling technique and are analyzed on-line by gas chromatography with flame ionization detection (GC/FID). The total weight in pounds or kilograms of EO is calculated using the measured EO concentrations and the measured temperatures, flow rates, and pressures of the sampled stream.

APPARATUS

The following equipment is required for performing semi-continuous direct sampling with on-line GC/FID analysis.

Heat-traced Teflon® Line

A heat-traced Teflon line is used to transport the sample from the vent stream to the gas sampling valve of the GC. The line is heated to a temperature slightly higher than the temperature of the vent gas in order to prevent condensation. The length of line required depends upon the proximity of the GC to the sampling port.

Pumps

Two vacuum pumps are required. One pump, capable of pumping 1 liter per minute (L/min) [0.035 cubic feet per minute (cfm)] with a leak-free, Teflon-coated diaphragm, is used to continuously withdraw sample from the sampling port and to pump sample to the gas sampling valve of the GC. The other pump, capable of pumping 100 milliliters per minute (mL/min) [0.0035 cfm] is used to flush the sample loop.

Acid Scrubbers

Two 500 mL Erlenmeyer flasks with two-hole stoppers containing dilute sulfuric acid at a pH of 1 are used to remove EO from the sampling stream and the GC slip stream before venting them to the atmosphere. The acid scrubbers may not be required when sampling controlled emissions if the exhaust lines are vented in a well-ventilated area void of personnel.

Thermocouples

Two thermocouples are needed to monitor the temperature of the vent stream. One should be wrapped in moist material to measure the wet bulb temperature. The accompanying temperature readout devices should be capable of measuring from ambient temperature up to 200°F (93°C).

Restricted Orifice Plates and Flanges

Restricted orifice plates sized to the vent are needed to monitor the flow rate of the vent stream. Standard orifice flange plates and flanges with standard pressure taps are recommended. If CFC-12 is used in the sterilant gas, two orifice plates are required.

Vane Anemometer

A vane anemometer is needed to measure gas stream linear velocites between 20 and 150 ft/min (6-45 m/min). A digital vane anemometer capable of measuring velocity at 10-sec intervals and with an ouput jack for a strip chart recorder is recommended.

Gas Chromatograph with Flame Ionization Detectector(FID) and Heated Gas Sampling Valve

A GC with a sampling valve, column, and detector is needed for the semi-continuous analysis of the vent sample. Other detectors (Thermal

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Conductivity Detector or Photoionization Detector) may be substituted for the FID if they are shown to give equivalent results.

Chromatographic Column

A stainless steel, 10 foot (ft) [3 meter (m)] x 1/8 inch (in) [3 millimeter (mm)] outside diameter (O.D.), column containing 5% Fluorcol on 60/80 mesh Carbopack B is used to separate the EO from the CFC-12 and other materials present in the vent gas. Other columns (Chromosorb 102, Porapak® Q or R, Carbowax 20M) may be used, provided that the precision and accuracy of the standards analysis are not impaired. Information confirming that adequate resolution of the EO peak must be presented. Adequate resolution is defined as an area overlap of not more than 10% of the EO peak by an interferent peak.

Recorder/Integrator

A recorder/integrator is needed to record results.

Flow Meter

A flow meter is needed to accurately monitor sample loop flow rate of 100 mL/min.

Regulators

The following regulators are required for the GC support gases and the EO standards.

CGA 580--

One regulator is needed for the nitrogen carrier gas. A second regulator may be required for the standard manifold purge if the carrier gas line cannot be tapped.

CGA 590--

One regulator is needed for the air for the FID.

CGA 350--

Five regulators are needed; one regulator for the hydrogen on the FID and four regulators for the EO and CFC-12 standards. Two regulators with stainless steel diaphragms and Teflon seats and seals are required for the low concentration standards; one should be reserved for standards under 20 ppmv EO and the other for standards between 20 and 800 ppmv EO. The other two standard regulators must be stainless steel; one should be reserved for standards between 800 ppmv and 2.5% (v) and the other for standards above 2.5% (v).

Teflon Tubing

Teflon tubing is needed to connect the gas cylinders to the GC, the sample loop to the sampling line and standard cylinders, the sampling line to the exhaust area, and for other miscellaneous connections. The diameter and length of the tubing depend upon the requirements of the system used. A recommended amount and diameter of tubing would be 10-20 ft (3-6 m) of 1/4 inch O.D. tubing. Each standard regulator should be equipped with 4-5 ft (1-2 m) of 1/8 in O.D. Tefon tubing.

Fittings

An assortment of Swagelock® fittings is desirable to plumb the GC to the gas cylinders and the sampling line to ensure leak-tight fittings. The size and type of fittings needed depend upon the type of tubing used and the type of fittings required by the GC and the cylinder regulators. Some recommendations are:

Caps and Front and Back Ferrules--

Teflon caps and ferrules (1/4 in) are needed to plumb in the glass flask. Stainless steel caps and ferrules (1/4 in and 1/8 in) are used on the ends of the Teflon tubing.

Unions--

Teflon (1/4 in) and stainless steel (1/4 in and 1/8 in) unions are used to connect tubing to impingers, sampling valves, etc.

Reducing Unions--

Stainless steel reducing unions (3/8 in to 1/4 in and 1/4 in to 1/8 in) are needed to connect cylinders to the GC and the sampling line to the gas sampling valve.

Soap Film Flow Meter

A soap film flow meter is used to measure GC carrier and support gas flow rates. It is also needed to calibrate any rotameters, dry gas meters, and mass flow meters used.

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Two- or Three-way Radio

A two- or three-way radio is helpful to simplify communications between personnel at the sampling port, in the analytical area, and in the sterilizer control room.

REAGENTS

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available; otherwise, use the best available grade.

Nitrogen Gas

A grade of nitrogen which is 99.995 percent pure is required for use as the chromatographic carrier gas and as the system blank. If lower grades of nitrogen are used, purify the gas using hydrocarbon, water, and oxygen traps.

Hydrogen Gas

A grade of hydrogen which is 99.995 percent pure is required as a support gas for the FID. If lower grades of hydrogen are used, purify the gas using a hydrocarbon trap.

Air

A grade of air which is 99.9999 percent pure is required as a support gas for the FID. If lower grades of air are used, purify the gas using a hydrocarbon trap containing activated carbon.

Ethylene Oxide Standard Cylinders

Ethylene oxide and CFC-12 standards prepared in nitrogen which are certified through direct analysis are recommended for system calibration. The following concentrations balanced in nitrogen are suggested:

- 30% (v) EO and 5% (v) CFC-12,
- 3% (v) EO and 4000 ppmv CFC-12,
- 0.3% (v) EO and 300 ppmv CFC-12,
- 400 ppmv EO and 70% (v) CFC-12,
- 40 ppmv EO and 5% (v) CFC-12,
- 5 ppmv EO and 4000 ppmv CFC-12,
- 0.5 ppmv EO and 300 ppmv CFC-12.

If testing is performed on a controlled outlet only, the percent level EO standards are not needed.

1 N Sulfuric Acid Solution

A scrubbing solution consisting of 1 N H_2SO_4 with a pH between 1 and 2 is required for removing EO from the sampling stream before venting to the atmosphere. To prepare add 30 mL of concentrated sulfuric acid to 1 L of distilled water. Mix well. A minimum of 500 mL of scrubbing solution is needed.

Quality Assurance Audit Samples

Audit samples as described in Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis," 40 CFR, Part 61 are required.

PROCEDURE

Sampling Considerations

The sampling period begins with the start of the initial chamber evacuation and ends at the completion of the final air wash. The sampling line is continuously flushed with sample during the sampling period. The number of GC injections is based on the resolution time of the chromatographic column and the length of the evacuation interval.

Flow Rate Determination--

Restricted orifice plates are used as the basis for determining the stack gas velocity and the volumetric flow rate of the sample stream at linear velocities above 150 ft/min (45 m/min). This method calls for the use of orifice plates sized to the vent and fitted in flange holders with standard pipe taps. In cases where the gas density varies significantly two orifice plates may be required. At linear velocities between 20 and 150 ft/min (6-45 m/min) the method calls for the use of a vane anemometer.

Temperature--

Record temperature every 2 min with a type-K thermocouple or equivalent.

Moisture Content--

Determine the moisture content of the vent stream using the wet bulb/dry bulb technique.

Semi-continuous Direct Sampling Procedure

In this procedure, sample is continuously withdrawn from the vent stream using a vacuum pump. A slip stream of gas is channeled into the gas sampling valve and injected into the chromatograph at 4 min intervals.

Assemble the sampling system as shown in Figure 1. Adjust the needle valves to yield a flow rate of 1 L/min to the manifold and 100 mL/min to the GC gas sampling valve. Leak check the assembly to prevent sample dilution and to protect personnel from fugitive EO emissions.

Place the probe at the centroid of the stack. Start the vacuum pumps and heat the sample transfer lines to prevent condensation.

When evacuation of the chamber begins, record the vane anemometer reading and the temperature of the vent gas at 2 min intervals. During the first and second evacuations measure oxygen content at 1 min intervals during the first 7 min of the evacuation. Measure oxygen content at least once during any subsequent evacuations. Take at least one wet bulb reading during each evacuation.

Analytical Procedure

A slipstream of the sample stream is drawn through a gas sampling loop and injected into a GC at 4 min intervals.

Gas Chromatographic Conditions--

The chromatographic conditions listed in Table 1 will resolve EO from CFC-12 and other interferences common to EO sterilization chamber vents. It may be necessary to change these conditions to resolve other interferences that are present in samples collected from different EO sources.

Calibration--

Calibrate the GC before the start and at the end of the test using the gas standards. A minimum of four points (four different standard concentrations) are needed to construct a calibration curve. For analysis of samples from an uncontrolled chamber, the GC needs to be calibrated with 400 ppmv to 30% (v) EO standards. For analysis of samples from a controlled chamber, the GC requires calibration with 0.5 ppmv to 400 ppmv EO standards. Use the same injection method and the same volume of sample for the calibration standards and the samples.

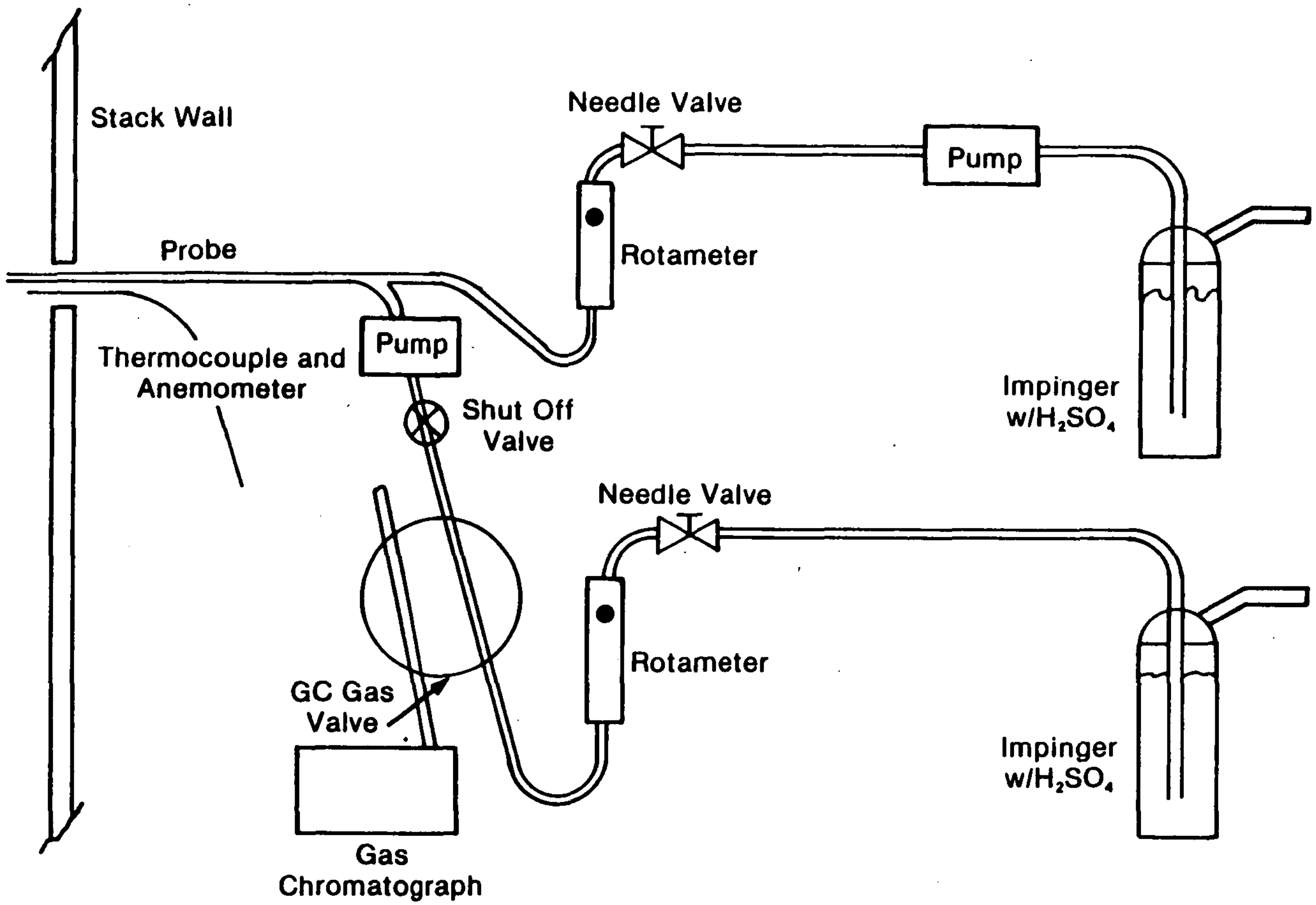

Figure 1. Semi-Continuous Direct Sampling System Assembly

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TABLE 1. GAS CHROMATOGRAPHIC CONDITIONS

Parameter	Recommendation
Column	5 percent Fluorcol on 60/80 Mesh Carbopack B, 10 ft (3 m) x 1/8 in (3 mm), stainless steel
Column Temperature	55^{o}C, isothermal for percent level analyses; 65^{o}C, isothermal for ppmv level analyses
Injector Temperature	200^{o}C
Detector Temperature	250^{o}C
Gas Flow Rates	Follow manufacturer's recommendations
Valve	6-port heated to 150^{o}C
Sample Loop Size	0.5 or 1 mL

Sample Analysis--

After the chamber evacuation begins, prepare to acquire the first sample. Before making the initial injection, allow sufficient time (3-4 min) for the residual air to purge from the line and for the sample to reach the manifold. (The time required will vary depending upon the amount of line used and the distance between the sampling port and the chromatograph. Determine sample line residence time prior to the test period.) Purge the sample loop for a minimum of 20 sec, simultaneously close the sampling valve and disconnect the vacuum pump, allow the sample loop to reach atmospheric pressure and make the initial injection. After the initial injection, make subsequent injections at 4 min intervals until the chamber evacuation ends.

Documentation--

Document each chromatogram by listing the sample location, injection volume, and injection time.

Audit Analysis

Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis." 40 CFR, Part 61.

CALIBRATION

Rotameter

Calibrate the rotameter at three different flows before and after each test.

Probe Temperature Gauge and Thermocouple

Calibrate using ice water and boiling water (ASTM-E1 #63C or 63F specifications) before the test.

Restricted Orifice Plates and Pressure Transducers

The restricted orifice plates should be purchased calibrated in the range of expected use. The pressure transducers should be calibrated for the expected range before use in the field.

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Vane Anemometer

Provide factory calibration (or equivalent) of the vane anemometer in the range of expected use.

Gas Chromatograph

Calibrate the GC at the start and at the end of each test day using prepared or purchased gas standards. Follow the calibration procedure described earlier. Use the chromatographic data (peak height or area) and standard concentration to prepare a least squares calibration curve.

Certified Standard Cylinders

Verify the certified concentrations of the purchased standard cylinders using an independent standard (one purchased from a second supplier or prepared in the laboratory using pure EO and CFC-12 diluted with nitrogen). Using the independent standard, prepare four-point calibration curves. From the calibration curves, calculate the measured concentrations of the certified standards. If the measured concentrations differ from the certified concentrations by more than $\pm 10\%$, do not use the standards.

CALCULATIONS

Perform the following calculations, retaining at least one figure more than the required number of significant figures. Round off to the correct number of significant figures after making the final calculation.

Ethylene Oxide Concentration

Determine the EO concentration at each measured point by comparing the peak area obtained for each sample with those derived from the least squares calibration curve obtained as described earlier. Plot EO concentration versus elapsed time.

Inert Gas Concentration

Determine the inert gas concentration at each measured point based on GC data. If no CFC-12 is present in the sample, assume the gas which is not EO is air. Plot the inert gas concentration versus elapsed time.

Moisture Content

Calculate the moisture content (C_a) in the exhaust gas using the following formula:

$$C_a = (VP \times RH)/P_{bar} \qquad \text{(Equation 1)}$$

where:

C_a = Water vapor in the gas stream, mole fraction
P_{bar} = Barometric pressure, mm (inches) Hg
VP = Saturated vapor pressure of water at stack temperature, mm (inches) Hg
RH = Relative humidity determined by wet bulb/dry bulb method

The relative humidity using the wet bulb/dry bulb method and the saturated vapor pressure of water at stack temperature can be obtained from standard tables.[15, 16]

Molecular Weight of the Gas

Determine the molecular weight of the gas at each measured point using the following formula:

$$MW_{av} = P_{EO} \times 44.05 + P_F \times 120.91 + P_A \times 28.975 + P_W \times 18.02 \qquad \text{(Equation 2)}$$

where:

MW_{av} = Average molecular weight, g/g-mole (lb/lb-mole)
P_{EO} = Volume Percent EO
P_F = Volume Percent CFC-12
P_A = Volume Percent air
P_W = Volume Percent water

Total Gas Flow Rate

Calculate the total flow of gas emitted in terms of pounds per second (lb/sec [kilograms per second (kg/sec)]) at each measured point using the following equation:[17]

$$w = KYA \quad (2g_c(p_1 - p_2)\,\rho\,)^{1/2} \qquad \text{(Equation 3)}$$

where:

A = cross-sectional area of the orifice throat, ft^2,
w = mass rate of flow, lb/sec,
K = $C/(1-B^4)^{1/2}$, dimensionless,
C = coefficient of discharge, dimensionless,
B = ratio of throat diameter to pipe diameter, D_2/D_1, dimensionless,

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D_2 = orifice throat diameter, in,

D_1 = pipe diameter, in,

Y = expansion factor, dimensionless,

g_c = dimensional constant = 32.174 (lb ft)/(lb force sec^2),

p_1, p_2 = pressure at upstream and downstream static pressure taps respectively, lb/ft^2, and

ρ = density at upstream pressure and temperature, lb/ft^3.

Values for C may be obtained from Reference 17. Determine the expansion factor, Y using the equation:[17]

$$Y = \{r^{2k}[k/(k-1)][(1-r^{(k-1)/k})/(1-r)][(1-B^4)/(1-B^4 r^{2/k})]\} \qquad \text{(Equation 4)}$$

where:

$r = p_2/p_1$,

k = specific heat ratio, C_p/C_v.

Values for k may be obtained from the appropriate figures in Reference 18. Plot a graph of total gas flow rate versus elapsed time.

Ethylene Oxide Mass Flow Rate

Select a number of points at equal time intervals during the evacuation. At each selected point combine total gas flow rate, vent gas molecular weight, and EO concentration at that point using the following equation:

$$m = 60 \times w \times (P_{EO} \times MW_{EO})/MW_{av} \qquad \text{(Equation 5)}$$

where:

m = mass flow rate of EO, lb/min,

w = total gas flow rate, lb/s,

P_{EO} = EO concentration, percent by volume = ppmv/10^6,

MW_{av} = molecular weight of the vent gas, and

MW_{EO} = molecular weight of EO.

Plot a graph of EO mass flow rate versus elapsed time.

Total Mass of Ethylene Oxide

Integrate the curve obtained above to determine the total weight of EO exhausted to the atmosphere during the post-sterilization period. Add the weights determined for the individual evacuations to obtain the total weight of EO emitted over the entire exhaust cycle using the following equation:

$$\sum_{i=1}^{k} \overline{M_i} \; t = \text{total mass} \qquad \text{(Equation 6)}$$

where:

- i = The equally spaced time interval
- k = Number of time intervals
- $\overline{M_i} = (M_{i-1} + M_i)/2$
- M_i = Mass flow rate, lb/min
- t = Time interval, min

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SECTION 5

LABORATORY METHOD EVALUATION AND OTHER EXPERIMENTS

SUMMARY OF LABORATORY STUDIES

The following tasks were performed in the laboratory and are reported below:

- A semi-continuous direct sampling method and a canister sampling method were tested on an artificially generated vent stream;
- The stability of EO standards in Summa® canisters was determined and a method of removing residual EO from the canisters was evaluated;
- A sample of vent gas taken during the pretest survey at the chosen facility was analyzed in the laboratory;
- Different packed columns were evaluated to determine their suitability to separate EO and CFC-12;
- Adsorption of EO on the sample loop and other surfaces was determined;
- The retention time shift of the EO peak on the column of choice was studied; and
- A sample of vent gas was analyzed by gas chromatography with mass spectral detection (GC/MS) and with flame ionization detection (GC/FID).

VENT STREAM TESTING

A pseudo-EO chamber vent stream was produced and the necessary sampling equipment was assembled in the laboratory. The testing system performance was checked for reproducibility. A semi-continuous direct and a canister sampling method were tested for accuracy using the assembled system.

The semi-continuous direct sampling method with on-line gas chromatographic analysis was tested because of its rigor. This method should provide accurate emissions data regardless of the EO concentration profile of the exhaust stream. However, this method has several disadvantages. First, it requires on-site analysis. Second, each sample can only be analyzed one time since sampling and analysis are performed on-line. Finally, the number of samples acquired is limited by the analysis time of the sample on the column.

Using grab sampling or integrated grab sampling eliminates some of these disadvantages. The collection of integrated grab samples in canisters has the advantages that collected samples can be shipped to a laboratory for later analysis and that multiple injections can be obtained for each sample. The major problem with canister sampling is that it is a time-integrated method and will only provide accurate emission measurements if the EO concentration profile of the exhaust stream is static.

Canisters were chosen instead of Tedlar® bags as the collection container for integrated samples because canisters are sturdy containers which have a lower potential for leaking. Ethylene oxide has the potential to cause chromosomal damage at levels of 50 ppmv and to increase the risk of leukemia at levels of 20-30 ppmv.[5] Using canisters would help to minimize worker exposure to EO.

Description of the Testing System and Sampling Setup

Several simulated EO chamber vent and sampling configurations were tested. The final configuration is shown in Figure 2. The dry gas meter was placed after the sampling port so that it would not interfere with concentration determinations. The EO chamber vent was simulated using a cylinder of 50 ppmv EO standard in nitrogen, a nitrogen cylinder, and calibrated Tylan flow controllers. The sampling system consisted of a needle valve, Thomas pump, and either a gas sampling loop or a Summa canister.

Both the flow rate and concentration of the vent stream were adjusted to simulate a reduced, yet similar, flow and concentration pattern which would occur from a large (1000 ft^3 [28 m^3]) sterilizer. Two different flow and concentration patterns were used, one to simulate an initial chamber evacuation and the other to simulate a subsequent evacuation.

Testing System Reproducibility

The EO and nitrogen flow rates were varied at 30-second (sec) intervals. The set flow rates were recorded after every adjustment or 30-sec interval. Using the recorded set flow rates, the total weight of EO emitted from the simulated vent was calculated. The relative standard deviation in total

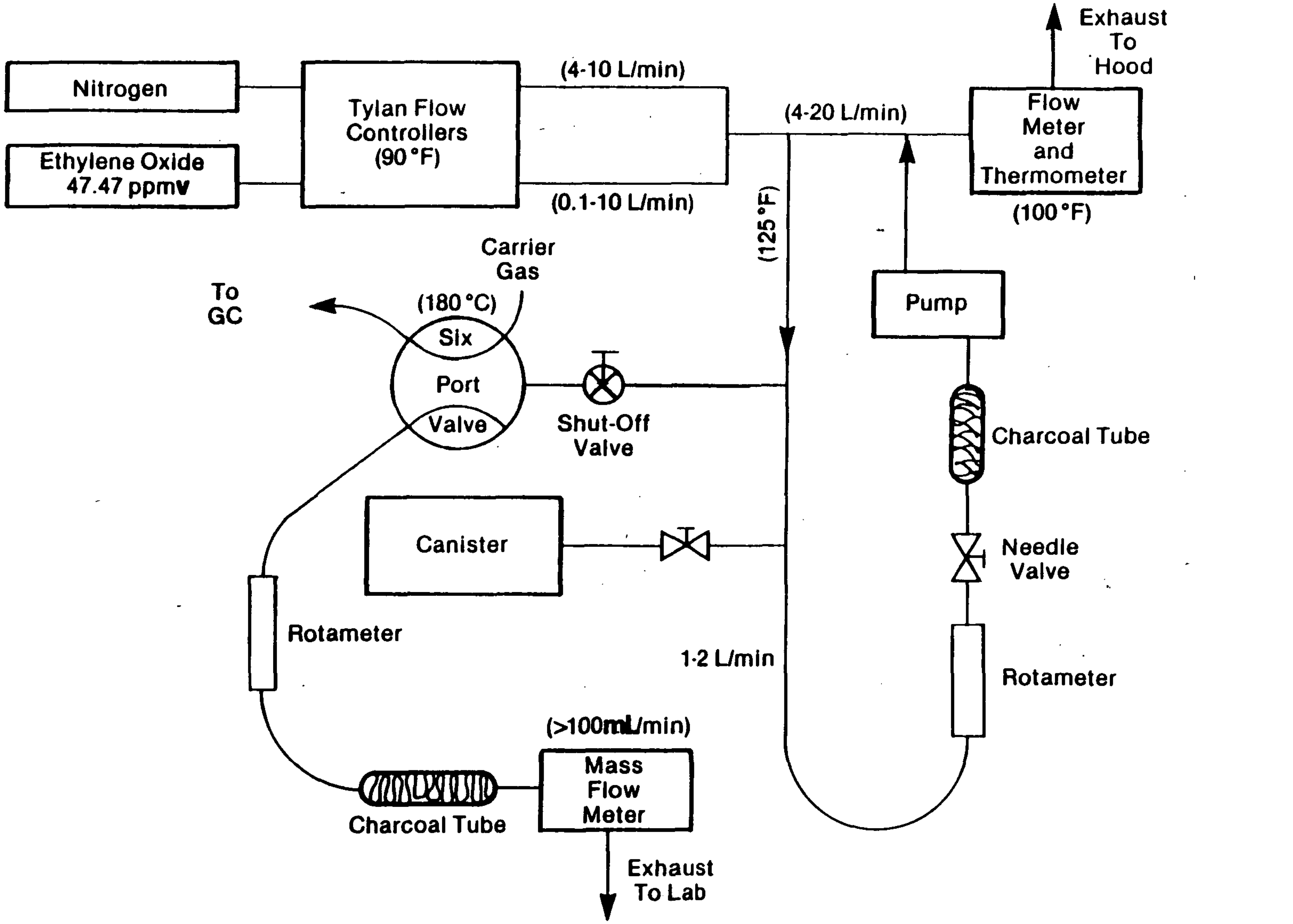

Figure 2. Laboratory Test System

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milligrams of EO emitted between simulations was <1 percent. Thus, the vent simulator generated reproducible variable flow and variable concentration patterns for evaluating both sampling methods.

Results of the Semi-continuous Direct Sampling Method

Semi-continuous direct sampling was evaluated in the laboratory as a method of measuring EO emissions from a variable flow and variable concentration vent. The vent flow rate was recorded every 30 sec. Initially, the gas sampling valve was flushed for a minimum of 30 sec. Samples were injected into the gas chromatograph when the pressure within the loop reached atmospheric pressure. After the initial sample injection, samples were taken every 1.5 to 2 min by closing the gas sampling shut-off valve.

Three trials using semi-continuous direct sampling were conducted. Each trial consisted of an initial evacuation and an air wash simulation. In all three trials the measured emitted mass of EO was within 11% of the expected value. The between-trial precision, as measured by relative standard deviation, was 5 percent.

Results of the Canister Sampling Method

Canister sampling was evaluated in the laboratory as another method of measuring EO emissions from a variable flow and variable concentration vent. The vent flow rate was recorded every 30 sec. The canisters were filled at a constant rate of 500 mL/min (0.0018 cfm). The canister samples were injected into the gas chromatograph at the completion of the vent simulation.

Two trials using canister sampling were conducted. No additional trials were performed because the results of the method were reproducible. Each trial consisted of an initial evacuation and an air wash simulation. In both trials the total measured emitted mass of EO was within 15% of the expected value. The relative difference (given by the difference in the two values divided by the mean) between the two trials was <5 percent.

CANISTER STUDIES

In order to propose a viable canister field sampling method in the future, both the stability of EO in the canisters and a method of removing residual EO from the canisters were determined.

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Stability Studies of EO in Summa Canisters

The stability of EO in nitrogen in 6 liter (L) [0.2 ft^3] Summa canisters was studied over a two-month period. Two canisters were used for the study. One canister was filled with a 98.05 ppmv EO standard in nitrogen and the other canister was filled with a 4.454 ppmv EO standard in nitrogen. Both EO standards were certified to within ± 2 percent.

The standards in the two canisters were analyzed throughout a two month period using GC/FID. The response of the standards in the canisters was compared to the response of the standards in the original aluminum cylinders. The results are shown graphically in Figure 3. The graph was prepared by taking the difference between the response of the sample in the canister and the response of the standard, dividing it by the response of the standard and multiplying it by 100. Numbers closer to zero indicate greater stability.

No degradation or loss of EO was observed during the first 24 hours. After three days (72 hours), the 4.454 ppmv EO standard showed a loss of approximately 7 percent. A maximum loss of 40% occurred within a one month (29 day) period. No additional loss in the low concentration standard was observed after one month (between 29 and 65 days). The 98.05 ppmv EO standard showed a 2.5% loss over the two-month (65 day) period.

The loss of EO in the Summa canisters was attributed to adsorption of the EO onto the surface of the canisters. The amount of EO adsorbed on the surface of the canisters was equivalent to approximately 2.5 ppmv. This value was obtained from the loss of approximately 50% of the 4.454 ppmv standard and approximately 2.5% of the 98.05 ppmv standard. A 0.5 ppmv EO standard was prepared in a canister that had been previously exposed to EO. Its response on the GC/FID was compared to the response of the certified 4.454 ppmv standard. After one week, the response ratio of the two standards had not changed. From this limited study of three canister samples, the following recommendations can be made:

- If possible, all EO samples collected in Summa canisters should be analyzed within one week of collection.
- Summa canisters, used to collect EO samples which are expected to be 2.5 ppmv or less, should be pre-exposed to EO before sampling.
- Additional studies regarding the stability of EO samples from actual sources in Summa canisters should be conducted.

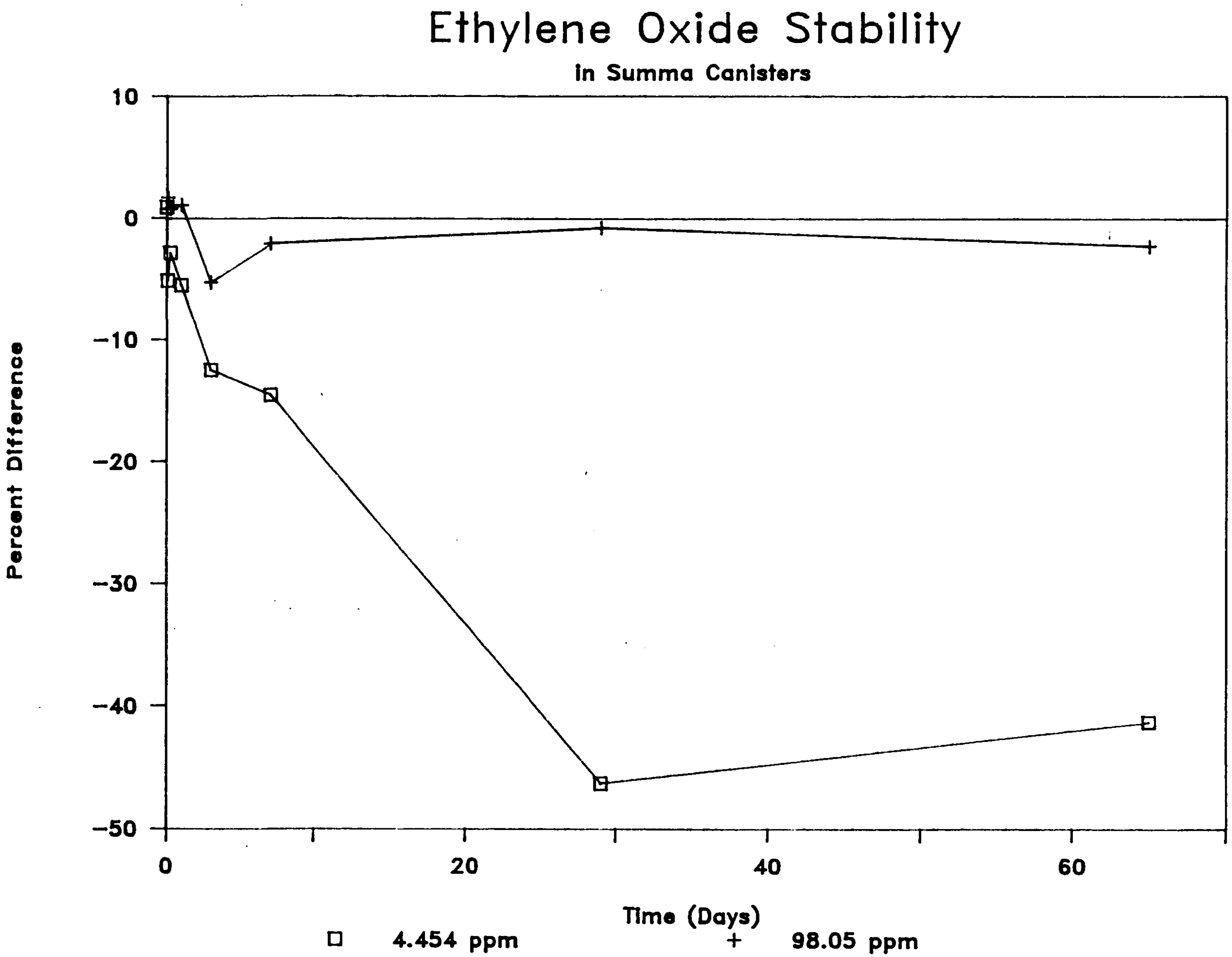

Figure 3. Ethylene Oxide Stability In Canisters

Residual Canister Cleanup

A method for cleaning the canisters in the field was developed and tested in the laboratory. Filling the canisters with clean nitrogen three times was found to be inadequate to remove the residual EO. As much as a third of the original EO remained in the canister. However, when the canister was evacuated with a vacuum pump between each of the three nitrogen purges, all of the residual EO was removed.

ANALYSIS OF PRESURVEY SAMPLE

In September 1986, Burron Medical in Allentown, Pennsylvania was selected as a field test site for evaluation of the semi-continuous direct sampling and analytical method. A pretest site survey was performed to verify the suitability of the site for the method evaluation.

During the survey, eight grab samples were obtained from the control unit stack, six in Vacusampler® cans and two in stainless steel bombs. Five of the samples (three cans and both bombs) were returned to Radian for analysis and three were analyzed by the facility. The samples were obtained during the first chamber evacuation of a normal product sterilization cycle.

The samples returned to Radian were analyzed by GC/FID using both a Porapak® R column and a 1% SP-1000 on Carbopack B column. Both were 6 ft (3 m) by 1/8 in (3 mm) O.D. stainless steel columns. On the Porapak R column the EO eluted after 4 min and the CFC-12 eluted at 2.7 min at a column temperature of 100°C. On the SP-1000 column the EO eluted at 1 min and the CFC-12 eluted at 1.9 min at a column temperature of 60°C.

The EO on the Porapak R column was well resolved from the CFC-12 when moderate amounts of CFC-12 were present; however, when the sample consisted of primarily CFC-12, the EO was lost in the CFC-12 tail. Quantitation of the EO in any of the samples was difficult on the Porapak R column.

The SP-1000 column easily resolved the EO from the CFC-12 and the EO was easily quantitated for all of the samples. The measured EO concentration in the five samples ranged from 0.2 ppmv to 2.3 ppmv.

The plant analyzed their three samples on a glass column packed with 0.8% Tetrahydroxyethylenediamine (THEED) on Carbopack C. The samples were found to contain from 1.6 to 220 ppmv EO.[19]

Analysis of the presurvey samples indicated that replicate samples analyzed using different analytical systems in different laboratories may vary greatly in analyzed concentration. Also, the presurvey sample analysis indicated that a column that eluted EO before CFC-12 would be preferable in the analysis of ppmv levels of EO in the presence of percent levels of CFC-12.

COLUMN EVALUATION

Several columns were evaluated by the EPA Project Officer in order to find a column on which EO eluted before CFC-12.

Columns Evaluated

The columns evaluated by the EPA Project Officer may be divided into three categories, those that did not resolve EO and CFC-12, those in which the CFC-12 eluted before the EO, and those in which the EO eluted before the CFC-12. The columns which failed to resolve EO and CFC-12 included a 6 ft (1.8 m) by 1/8 inch (0.3 cm) stainless steel column containing 10% SP-1000 on 80/100 mesh Supelcoport tested at $50^{o}C$ and $100^{o}C$, a 5 ft (1.5 m) by 1/8 inch (0.3 cm) stainless steel column containing 3.8% OV®-1 on Chromosorb® W HP tested at $70^{o}C$, a 10 ft (3 m) by 1/8 inch (0.3 cm) stainless steel 10% Dibutyl maleate on 60/80 mesh Chromosorb P and a 6 ft (1.8 m) by 1/8 inch (0.3 cm) column containing 7% Squalene on Chromosorb 750 tested at $40^{o}C$ and $70^{o}C$.[20]

The columns which eluted CFC-12 before EO can be divided into two categories, those with a liquid phase and those without. The columns without a liquid phase included a 6 ft (1.8 m) by 1/8 inch (0.3 cm) stainless steel column containing 100/120 mesh Porapak R tested at $100^{o}C$, a 6 ft (1.8 m) by 1/8 inch (0.3 cm) stainless steel column containing 60/80 mesh Chromosorb 101 tested at $40^{o}C$ and $100^{o}C$, a 6 ft (1.8 m) by 1/8 inch (0.3 cm) stainless steel column containing 60/80 mesh Chromosorb 102 tested at $100^{o}C$, and a 10 ft (3 m) by 1/8 inch (0.3 cm) stainless steel column containing 80/100 mesh Porapak QS tested at $100^{o}C$.[20] Resolution data of EO from CFC-12 for most of these columns are presented in Table 2.

Columns which contained a liquid phase and in which CFC-12 eluted before EO included a 10 ft (3 m) by 1/8 inch (0.3 cm) stainless steel 10% SP-2401 on 100/120 mesh Supelcoport tested at 30 and $50^{o}C$ and a 2 ft (0.6 m) by 1/8 inch (0.3 cm) stainless steel column containing 20% Dibutyl maleate on 40/60 mesh

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TABLE 2. RESOLUTION OF EO FROM CFC-12[20]

Column[a] Description	Length (ft) [m]	Temperature (°C)	Resolution (R)	Retention Time (min) EO	Retention Time (min) CFC-12
Porapak R	6 [1.8]	100	2.5	4.5	
Chromosorb 101	6 [1.8]	100	1.8	2.7	
Chromosorb 101	6 [1.8]	40	1.8	26	
Chromosorb 102	6 [1.8]	100	3.2	4.4	
Porapak QS	10 [3]	100		7.9	4.6
10% SP-2401	10 [3]	50		1.6	1.0
10% SP-2401	10 [3]	30		2.3	1.0
C_4 Maleate	2 [0.6]			2.1	0.4
Carbopack B HT	6 [1.8]	60	0.5[b]	2.3	
Carbopack B HT	10 [3]	70	c	3.6	4.5
Carbopack B HT	16 [4.8]			5.6	9.6
5% Fluorcol	10 [3]	30	3.1	3.3	6.8
5% Fluorcol	10 [3]	40	2.4	2.6	4.9

[a]All columns were of premium grade stainless steel with outer diameters of 1/8 inch (0.3 cm).

[b]Almost baseline resolution. The R value is misleading because of the large width of the CFC-12 peak.

[c]Baseline resolution.

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Chromosorb P.[20] Retention times for EO and CFC-12 on these columns are reported in Table 2.

Columns which resolved the EO from the CFC-12 and eluted EO before CFC-12 included 6 ft (1.8 m), 10 ft (3 m) and 16 ft (4.8 m), by 1/8 inch (0.3 cm) O.D. stainless steel columns containing 60/80 mesh Carbopack B HT and a 10 ft (3 m) by 1.8 inch (0.3 cm) O.D. stainless steel column containing 5% Fluorcol on 60/80 mesh Carbopack B.[20] Resolution and retention data for these columns is presented in Table 2. The Fluorcol column was determined to be the best of these four columns because the linear range of the EO calibration curve spanned the greatest magnitude and the Fluorcol column had the larger number of plates, 2560 plates compared to 1940 plates for the Carbopack B HT columns.[20]

Further Evaluation of the Column of Choice

The 10 ft (3 m) by 1/8 inch (3 mm) O.D. 5% Fluorcol on 60/80 Carbopack B stainless steel column was further evaluated by the EPA Project Officer to determine the optimal GC/FID conditions for the separation of EO from CFC-12 and the limit of detection (LOD) for EO.

Optimization of Instrumental Conditions--

A column temperature of 55^{o}C was required for baseline resolution of percent level mixtures of EO (4-30% [v]) and CFC-12 (96-70% [v]).[14] For ppmv level EO concentrations baseline resolution was achieved at a column temperature of 65^{o}C.[14] A van Deemter plot indicated an optimum flow rate of 30 mL/min.[14]

Sample loops of 0.5 and 1.0 mL and samples of EO/CFC-12 mixtures with no air present were used to determine the linearity of the FID response. Ethylene oxide response was linear up to 30% (v) EO at both sample volumes.[14] The CFC-12 response was linear from 70-100% (v) with the 0.5 mL sample loop, but with the 1.0 mL loop nonlinearity occurred above 90% (v) CFC-12.[14]

Detection Limit Determination--

The LOD was estimated using a procedure developed by Knoll[21] and by taking twice the noise level. Using the optimum conditions determined above for low levels of EO, the LODs were 0.03 and 0.07 ppmv for 1.0 and 0.5 mL sample loops, respectively.[14] Both methods of determinating LOD gave the same results.

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Retention Time Shifts--

The EO retention time was observed to be a function of the EO concentration. With a nitrogen carrier gas flow rate of 30 mL/min and a column oven temperature of 65°C, the retention time was 1.7 min for percent level samples versus 2.1 min for a 1.1 ppmv sample.[14]

ADSORPTION STUDIES

During the column evaluation performed by the EPA Project Officer, some of the EO adsorbed onto the sample loop. Also, a study reported in the literature,[22] indicated that adsorption of EO was greatly reduced by replacing stainless steel sampling loops with Teflon sampling loops. Since heated stainless steel sampling loops would be used in the field, laboratory studies were performed to determine if EO adsorption occurred on heated stainless steel loops. Additional studies were also conducted to determine if adsorption occurred in the heated Teflon lines that would be used as sampling lines to transport sample from the sampling ports to the GC.

<u>Procedure</u>

The heated gas sampling valve was flushed for 0.5 min with nitrogen or standard flowing at 100 mL/min. Samples were injected when the rotameter indicated that there was no flow through the loop.

Initially, the system was blanked with ultra high purity nitrogen. Then the standard was injected until three peaks with reproducible area (within 10%) were obtained. Next nitrogen was injected either until the peak was very small or had totally disappeared.

Three system configurations were tested. In the first system, the shut-off valve and metering valve were connected before the sampling valve by a length of stainless steel tubing. The cylinder regulator was connected to the shut-off valve by a length of 1/4 inch O.D. Teflon tubing. To switch from nitrogen to standard to nitrogen, the Teflon tubing was switched between the nitrogen regulator and the standard regulator.

In the second configuration, the shut-off valve and metering valve were connected after the sampling valve. The cylinder regulator was connected directly to the sampling valve using a length of 1/8 inch O.D. Teflon tubing.

Again, to switch from nitrogen to standard to nitrogen, the Teflon tubing was switched between the nitrogen regulator and the standard regulator.

The third configuration was the same as the second configuration except that two 1/8 inch O.D. lengths of Teflon tubing were used, one between the nitrogen regulator and sampling valve and the other between the standard regulator and sampling valve.

A 5.005% (v) EO standard was used in all three configurations. In the third configuration, a 4.454 ppmv EO standard was also tested.

A 100 ft (30 m) heat-traced line heated to >100°C was tested for adsorption of EO by purging the line with 4.454 ppmv EO standard and comparing the peak area measured to the peak area measured when the same standard was analyzed directly.

Calculations

The amount of adsorption occurring in the system was calculated by the ratio of the area of the EO peak for the first nitrogen injection to the average area of the three standard peaks.

Results

The results of the sample loop adsorption studies are reported in Table 3. In Configuration 3 the adsorption measured was the adsorption occurring on the loop only. The amount of this adsorption was small compared to the adsorption measured in the other two configurations. For the high EO standard, the amount of adsorption was equivalent to 4.24 ppmv and for the low EO standard the amount of adsorption was equivalent to 0.1112 ppmv.

The amount of adsorption occurring on the Teflon line and in the loop was measured using Configuration 2. Approximately 4% of this adsorption could be attributed to the loop, so the amount of adsorption occurring on the surface of the Teflon line was equivalent to 99.4 ppmv.

The EO adsorption study on the heat-traced line was repeated twice. The absolute difference between the EO peak area obtained when standard was purged through the heat-traced line and the EO peak area when standard was analyzed directly ranged from -8.9 to 7.1 percent.

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TABLE 3. RESULTS OF ETHYLENE OXIDE SAMPLE LOOP ADSORPTION STUDIES

Configuration	Standard Concentration	Amount of Ethylene Oxide Adsorbed (In Terms of % of Average Standard Injection) 1 Purge	2 Purges	3 Purges
1	5.005% (v)	2.046%	0.569%	0.257%
2	5.005% (v)	0.207%	0.059%	0.032%
3	5.005% (v)	0.00847%	0.00428%	NA
3	4.454 ppmv	2.497%	1.411%	0%

Conclusions

The amount of adsorption occurring on the loop will not significantly affect concentration values for high concentration (>100 ppmv) EO samples. The effect of EO adsorbing on the loop will have a minimal effect on EO samples with concentrations between 10 and 100 ppmv. Sample loop adsorption effects will not become significant unless samples have concentrations below 1 ppmv; therefore, such designs are applicable for streams containing EO concentrations from 1 ppmv to 30 volume percent.

Some adsorption occurs in the Teflon lines between the standard cylinders and the sampling valve. To minimize any effect from EO adsorption on these surfaces, specific Teflon lines should be assigned to each regulator for use with that regulator only. Preferably each standard should have its own regulator or regulators should be used only on standards within a similar concentration range. Also, if possible, no metering valve or shut-off valve should be placed between the regulator and the sampling valve.

Adsorption losses of EO do not occur in the heat-traced sampling lines used to transport the sample from the sampling ports to the GC; therefore, such designs are applicable for streams containing EO concentrations from 1 ppmv to 30 volume percent.

RETENTION SHIFT STUDIES

In the initial study of the column, the EO retention time was observed to vary with the EO concentration. In the field, using a dual column instrument with one column dedicated for analyzing inlet samples and the other for outlet samples, the retention time was observed to shift on one of the columns but not on the other. Retention time shifts occurred when the carrier gas flow rate was less than 30 mL/min and the sample size was 2 mL. A carrier gas flow rate of about 60 mL/min and a 0.25 mL sample size caused minimal retention time shifts. To determine if the retention time shifts were a function of sample size or carrier gas flow rate, additional laboratory studies were performed.

Procedure

Ten standard samples, prepared gravimetrically in aluminum cylinders, were analyzed on the two 5% Fluorcol columns. Standard concentrations ranged from less than 1 ppmv to 12.5% (v). The carrier gas flow rates were maintained at less than 30 mL/min on one column (Column B) and about 60 mL/min on the other column (Column A). Two sample volumes, 2 mL and 0.25 mL, were injected on both of the columns. The column oven temperature was maintained at 100°C throughout the experiment.

Results

Each standard was injected twice under the four test conditions. Standard deviations from the two injections are reported in parentheses. At a high carrier flow rate and large sample volume the EO retention time shifted from 1.4 min (0.01) for a 4.5 ppmv standard to 0.9 min (.003) for a 12.5% (v) standard and the CFC-12 retention time shifted from 1.36 min (0) for a 1,200 ppmv standard to 1.14 min (0.004) for a 62.5% (v) standard. When the sample volume was decreased, the EO retention time shifted from 1.2 min (0.007) for a 9.1 ppmv standard to 0.8 min (0.01) for a 12.5% (v) standard and the CFC-12 retention time shifted from 1.21 min (0.02) for a 1,200 ppmv standard to 1.14 min for a 62.5% (v) standard.

A low carrier flow rate and large sample volume resulted in EO retention time shifts of from 2.6 min (0.04) for a 0.9 ppmv standard to 1.3 min (0.01) for a 12.5% (v) standard and CFC-12 retention time shifts of from 2.0 min (0.01) for a 1,200 ppmv to 1.6 min (0.01) for a 62.5% (v) standard. A decreased sample volume yielded EO retention time shifts of from 2.4 min (one injection only) for the 0.9 ppmv standard to 1.3 min (0.002) for the 12.5% (v) standard and CFC-12 retention time shifts of from 2.0 min (0.001) for the 1,200 ppmv standard to 1.8 min (0.003) for the 62.5% (v) standard.

For both compounds and both sample sizes the magnitude of the retention time shift is greater when the lower flow rate is used. There is no noticeable effect on the EO retention time shift due to sample size; however, the magnitude of the retention time shift increases with sample volume for CFC-12.

Retention Order Change and Coelution Possibilities

The shifting retention times raises a question regarding the conditions required for the compounds to coelute or change their relative retention characteristics. Figure 4 shows the EO and CFC-12 data plotted on the same

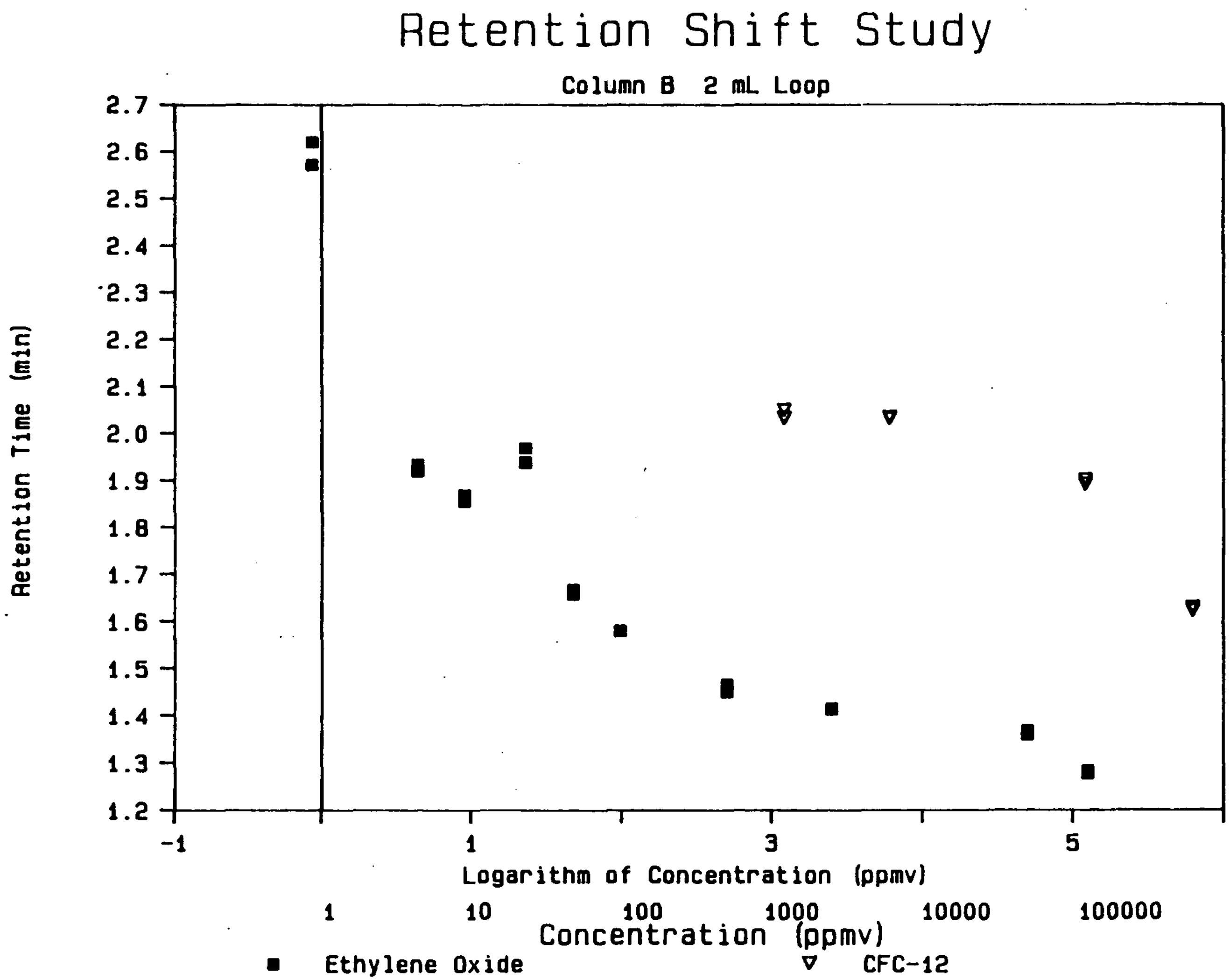

Figure 4. Retention Time Versus Logarithm of Concentration

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graph at low carrier gas flow and with a large sample volume. The natural logarithm of the concentration was used for plotting to allow all of the data to be plotted legibly on one graph. From this figure it is apparent that the CFC-12 retention time remains constant until the column is overloaded with sample. The EO retention time changes continually with concentration.

The plot also shows that there are many conditions under which the compounds would be expected to coelute. For example, in samples containing less than 10 ppmv of EO and less than 1% (v) of CFC-12, it is likely that the two components would coelute. Also, in a sample containing less than 100 ppmv of EO and more than 1% (v) CFC-12, it is possible that the order of elution would be reversed. These predictions are derived from the experimental data and need to be substantiated by experimentation to verify that there are no other parameters, such as column temperature or compound interactions, that affect the elution time and order.

Conclusions

The CFC-12 retention time probably remains constant until column overload begins at a concentration of approximately 1 volume percent. The EO retention time continually decreases with increasing concentration. For both compounds, the retention time shift with changing concentration is greater when the carrier gas flow rate is slower. A larger sample size does not increase the magnitude of the EO retention time shift but does increase the magnitude of the CFC-12 retention time shift.

The larger shift in EO retention times compared with the shift in CFC-12 retention times was due to the larger range in EO concentrations which were sampled. Also, the retention time shift was exacerbated relative for the laboratory results because of the higher column temperature used to obtain the needed number of samples.

ANALYSIS OF A VENT GAS SAMPLE IN THE LABORATORY

To verify the presence of EO in the scrubber outlet vent gas and to determine what other compounds are present in the scrubber outlet vent gas, a sample taken during Test 12, Evacuation 6, was analyzed by GC/MS and by GC/FID.

Analysis of Vent Gas Sample by GC/MS

The vent gas sample was analyzed by GC/MS to verify that EO was present in the vent gas during the later evacuations and to identify the other compounds in the vent gas which were interfering with the analysis.

Procedure--

One coil of a 30 meter (m) wide-bore fused silica capillary column (DB-5) was frozen with liquid nitrogen. A 1 mL gas sample was injected through the GC injection port which was heated to 50 degrees Celsius (^{o}C). Injection was made with the GC column oven door open. The door was closed, and the column oven was heated to 35^{o}C. After a two minute hold at 35^{o}C, the column oven was heated to 150^{o}C at 8^{o}C per minute. Both a 5 ppmv EO standard and the sample were analyzed.

Results--

Analysis of the 5 ppmv EO standard showed that the EO elutes at 2.47 min and yields a mass spectrum with a parent peak at mass 44 and a major peak at 29 due to the loss of a methyl group.

The sample chromatogram is shown in Figure 5. There are three peaks: a large one at 2.39 min, a small one at 3.12 min, and a medium one at 3.56 min. The mass spectra identify the first peak as CFC-12, the second peak as carbon disulfide (CS_2), and the third peak as 1,2-epoxybutane (ethyloxirane).

No EO was identified by this analysis. This was not unexpected, however. The estimated detection limit for the method was 1-2 ppmv, and the estimated concentration expected in the sample was 0.5-1 ppmv.

There is no explanation for the presence of the CS_2. The 1,2-epoxybutane may be a reasonable reaction product of the EO although its presence was not expected. At this time it is not known whether these products were materials actually present in the stack or whether they are artifacts formed when the sample contacted the sample container.

Conclusion--

By the sixth evacuation, the major component of the stack gas, other than air, is CFC-12. The concentration of EO has decreased to less than 2 ppmv. Other components present in the stack gas may include CS_2 and 1,2-epoxybutane (ethyloxirane).

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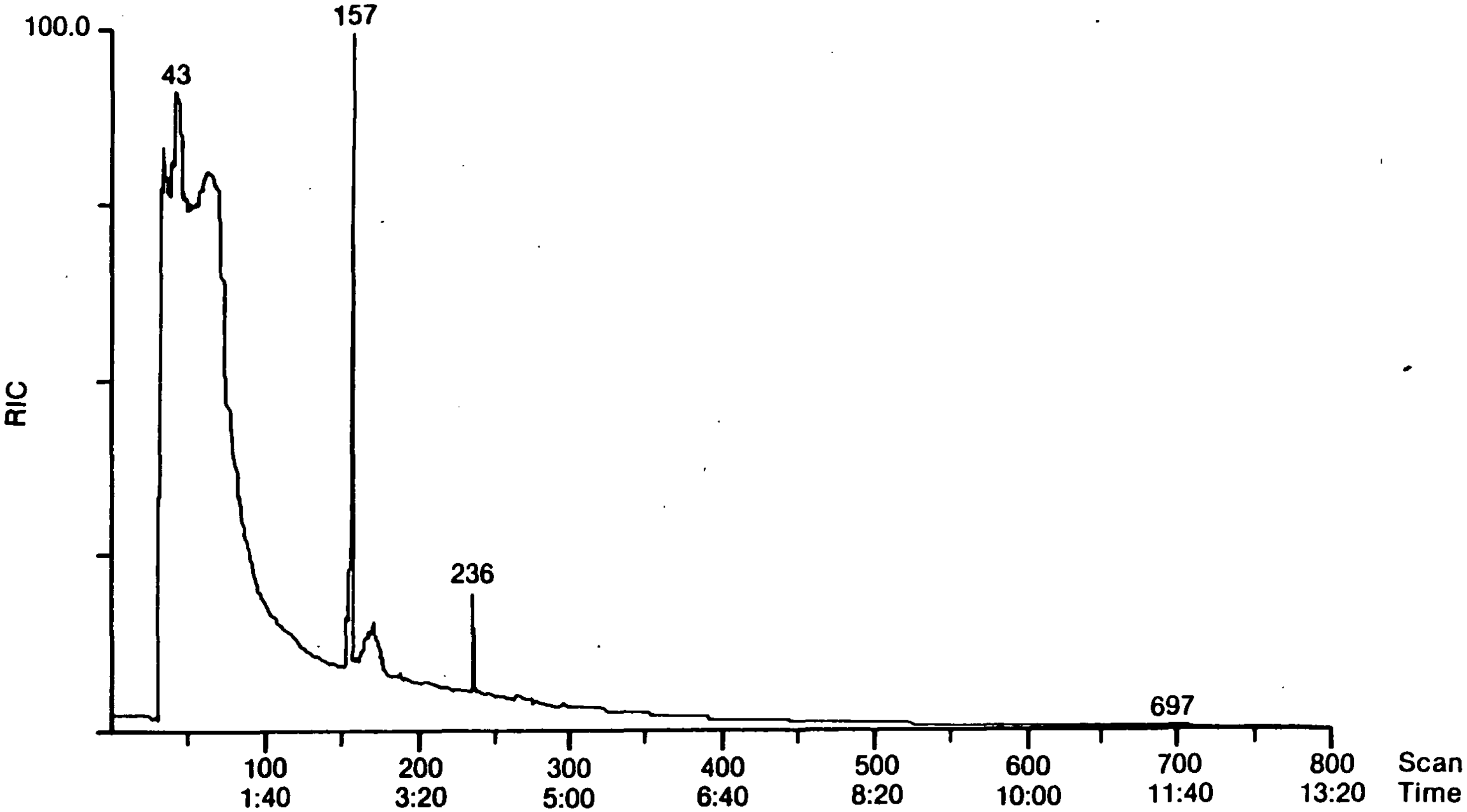

Figure 5. Total Ion Chromatogram of Vent Sample

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Vent Gas Analysis by GC/FID

The vent gas sample taken during Test 12, Evacuation 6, was analyzed by GC/FID using conditions similar to field conditions. Quantitative and qualitative comparisons were made to a standard containing EO, CFC-12, CS_2, and 1,2-epoxybutane.

Procedure--

A 2-L static dilution bulb was purged with 4.454 ppmv EO standard for 2 min. Using a syringe, 0.1 mL of CFC-12, 31.66 mg of CS_2 and 20.94 mg of 1,2-epoxybutane were added to the purged bulb. The bulb was stored in an oven at 60^oC. This resulted in concentrations of 4.454 ppmv EO, 50 ppmv CFC-12, 5,000 ppmv CS_2, and 3,600 ppmv 1,2-epoxybutane.

The sample prepared in the static dilution bulb, the 4.454 ppmv EO standard, and headspace samples of CS_2 and 1,2-epoxybutane were injected using a 0.5 mL gas-tight syringe on a 10 ft (3 m) by 1/8 in (3 mm) O.D. column containing 5% Fluorcol on 60/80 mesh Carbopack B. A Varian 3400 GC with a Vista 401 Data System was used. The column temperature was maintained isothermally at 100^oC; the injector block was heated to 175^oC, and the detector oven was maintained at 225^oC. A nitrogen carrier gas flow rate of 30 mL/min was used. Support gas flow rates were set at the manufacturer's recommendations of 30 mL/min for hydrogen and 300 mL/min for air.

Results--

Analysis of the individual components yielded retention times of 1.9 min for CFC-12, 2.2 min for EO, 4.8 min for CS_2, and 5.3 min for 1,2-epoxybutane. Using the sample prepared in the static dilution bulb, the limits of quantitation (LOQs) were estimated to be 1 ppmv for CFC-12, 1.5 ppmv for EO, and 10 ppmv for 1,2-epoxybutane. No LOQ was estimated for CS_2 because the 5,000 ppmv CS_2 in the static dilution bulb was not detected by the FID. No effort was made to determine a CS_2 detection limit.

Analysis of the vent gas sample yielded a chromatogram with one peak at 1.9 min. This peak was identified as CFC-12 and was estimated to be present at a concentration of approximately 500 ppmv. The presence of EO and CS_2

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could not be determined. Epoxybutane was estimated to be present at levels below the estimated LOQ of 0.01 ppmv.

Conclusions--

In a mixture containing 50 ppmv of CFC-12 and 5 ppmv of EO, the relative retention times of the two materials were reversed. Figures 6 and 7 show chromatograms taken during the field test at the inlet and outlet of the control unit, respectively. For the analysis of the inlet samples the carrier gas flow rate was faster and the sample volume was smaller. The late eluting component of the vent gas observed in the field at the scrubber outlet was probably 1,2-epoxybutane. This vent gas component required the analysis time to be lengthened on the outlet channel and decreased the number of samples which could be analyzed during each evacuation. Other unidentified components of the outlet vent stream elute before the CFC-12, possibly interfering with the EO analysis.

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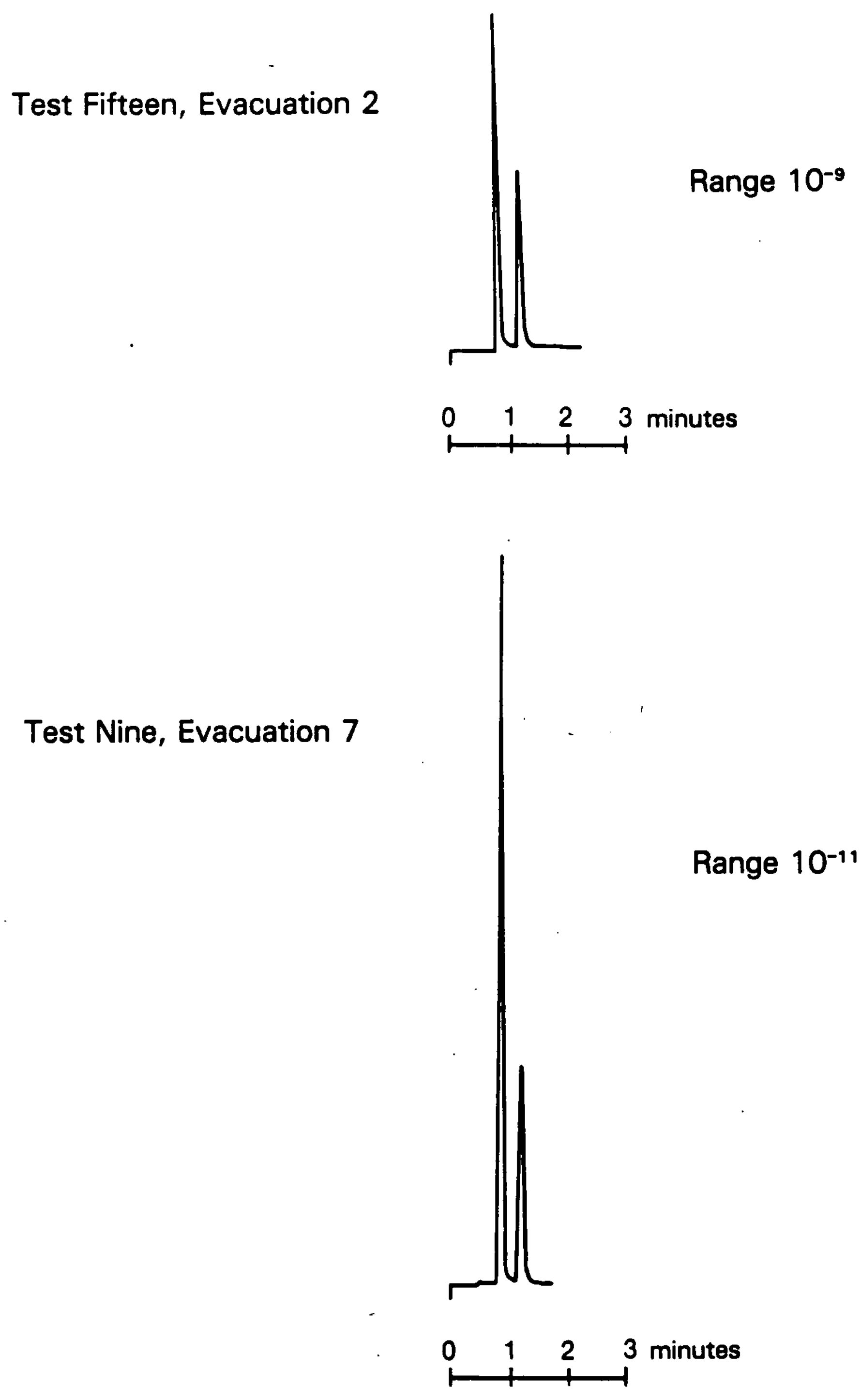

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Figure 6. Chromatograms of Vent Gas at Scrubber Inlet

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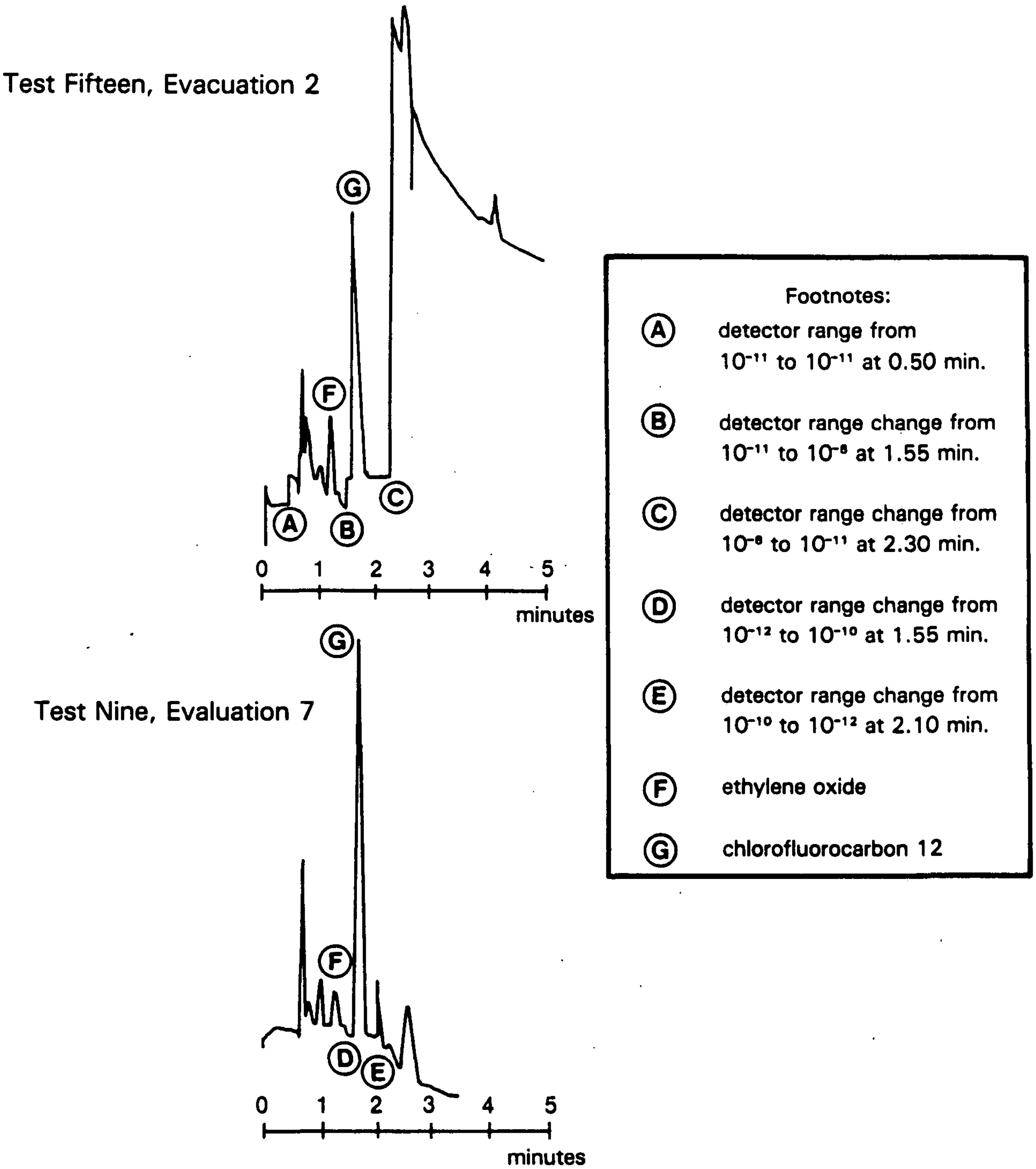

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Figure 7. Chromatograms of Vent Gas at Scrubber Outlet

SECTION 6

FIELD EVALUATION

FACILITY DESCRIPTION

The field evaluation was conducted at Burron Medical, a medical supply sterilization facility, located in Allentown, Pennsylvania. The facility has three 1000 ft^3 (28 m^3) sterilizers which use a 12/88 (w/w) EO and CFC-12 gas mixture. The gas is supplied from a common header serving all four units and is controlled by a liquid flow meter.

A sterilization cycle typically uses 38 gallons (140 L) of 12/88 gas mixture. On a weight basis, a sterilization charge consumes 368 lbs (167 Kg) of gas, of which approximately 44 lbs (20 Kg) are EO. The initial charge of EO to the chamber was calculated using the weight of the supply cylinders before and after charging the chamber. The scale measured the supply cylinders to ± 1 lb (0.5 Kg).

The exhaust from the sterilizers is controlled by a DEOXX™ system. The DEOXX system is a dilute acid scrubber manufactured by Chemrox, which hydrolyzes the EO to ethylene glycol. At the time of the test the scrubber contained a mixture of dilute phosphoric and sulfuric acid. The control system has a reported control efficiency of 99.99% based on tests conducted at the facility in April 1986 by the vendor.[12]

Each chamber is equipped with a total recirculating pump manufactured by either CIHI or Intervac. The pumps are equipped with gas/liquid separators which emit the gas to the DEOXX system and recirculate the liquid to the pump inlet. Chambers #1 and #2 are equipped with oil-sealed pumps. Chamber #3 is equipped with a water-sealed pump. All of the tests were conducted using the chambers (#1 and #2) equipped with oil-sealed pumps for the following reasons:

- The use of water-sealed pumps is more likely to affect EO emissions and efficiency calculations because of the infinite solubility of EO in water; and

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- The anticipated regulatory development will most likely require the use of oil-sealed pumps.

The sterilization cycle is automatically controlled by a programmable microprocessor system. The control system has the capability to control and record the parameters of the sterilization cycle including chamber temperature, chamber pressure, and elapsed time from the start of the cycle.

The sterilization process begins with a humidification step which takes place in a separate room. After the humidification step, each load to be sterilized is transferred to the sterilization chamber. The sterilization cycle is a batch process which takes 4-6 hr. A sterilizer load begun during the morning shift exhausts at about 2:00 p.m. In a typical plant operating mode seven post-sterilization evacuations occur over a 3 hr period. After the chamber repressurizes following the seventh evacuation, the product is removed from the chamber and allowed to off-gas. Because the control system is designed to handle the exhaust from two sterilizers venting simultaneously, the tested sterilization cycles were scheduled so that only one sterilizer vented at a time.

Three different sterilization programs were used for testing, one for the empty chamber tests, one for the full chamber tests, and one for the last full chamber test (Test 13). Before the start of every test (except Test 13), the chamber was evacuated to 2 pounds per square inch absolute (psia) and then pressurized to 3.1 psia with steam. The humidity dwell at 3.1 psia was maintained for 1 hr for the loaded chamber tests, but was shortened to 5 min for the empty chamber tests. At the completion of the humidity dwell the chamber was charged to 23.9 psia with 12/88 gas. The exposure at 23.9 psia was maintained for 4 hrs for the loaded chamber tests, but was shortened to 5 min for the empty chamber tests. During the last full chamber test (Test 13), the chamber was evacuated to 7 psia and pressurized to 32.9 psia.

Each program contained seven post-sterilization evacuations, the initial chamber evacuation and pump down and six air in-bleeds and subsequent evacuations, followed by a final air in-bleed. Except in Test 13, the chamber was evacuated to 2 psia and pressurized with air to 13.9 psia during each evacuation and air in-bleed cycle. The initial chamber evacuation and pump down lasted 26-27 min. The subsequent evacuations lasted 12-14 min and the air in-bleeds required 12-14 min. During Test 13 the chamber was evacuated to 7.0 psia, which reduced each evacuation and air in-bleed time by 7 min.

Seventeen tests were performed, five with product in the chamber and 12 without product. Data from ten of these tests were reduced and used to prepare this report. Table 4 summarizes the 10 tests that were used.

SAMPLING LOCATIONS

Samples were acquired at two locations, before and after the control unit. At the scrubber inlet the EO and CFC-12 concentrations were at percent levels and the sample temperatures were 40-50^{0}C (100-120^{0}F). At the scrubber outlet the EO concentrations were at the low ppmv level, CFC-12 concentrations were at the percent levels, and sample temperatures ranged from 30-70^{0}F (0-20^{0}C) depending on the ambient temperature at the time of the test.

Scrubber Inlet Sampling Location

The scrubber inlet sampling location, shown schematically in Figure 8, was used to obtain a continuous sample of sterilizer chamber exhaust. The exhaust was transferred from the chamber outlet to the scrubber inlet via a 6-inch diameter polyvinyl chloride (PVC) duct. Samples were taken from the midpoint between the sterilizer outlet and the scrubber inlet. Sample, acquired with a 3/16-inch Teflon probe, was transported to the GC through 50 ft 0.5 m) of 1/4-inch O.D. heated Teflon sample line. No direct flow measurements were made at this location because the installation of orifice plates in the existing PVC pipe was not considered to be cost-effective.

Scrubber Outlet Sampling Location

A continuous sample of scrubber exhaust was obtained and volumetric flow measurements were made at the scrubber outlet sampling location. Exhaust exited the scrubber vertically through a 6-inch diameter PVC ductwork that exhausted 5 ft (1.5 m) above roof level. To measure volumetric flow, the stack was modified by the installation of:

- additional 6-inch diameter PVC ductwork to allow for diversion of the scrubber exhaust through one of two parallel ducts,

TABLE 4. TEST SUMMARY

Test Number	Product Present	Chamber Number	Weight 12/88 Used	Test Date	Test Start Time	Test End Time
6[a]	Yes	2	368 lb	87/10/06	21:39	00:38
7[b]	No	1	365 lb	87/10/07	10:19	14:04
8[a]	Yes	2	388 lb	87/10/07	15:10	18:11
9[b]	No	1	346 lb	87/10/08	09:25	12:42
10[b]	No	1	353 lb	87/10/08	14:41	17:48
11[a]	Yes	2	392 lb	87/10/08	18:00	21:01
12[b]	No	1	346 lb	87/10/09	12:44	15:53
13[c]	Yes	2	442 lb	87/10/09	16:16	18:03
14[b]	No	1	350 lb	87/10/10	08:54	12:01
15[b]	No	1	343 lb	87/10/10	13:35	16:43

[a]The chamber was evacuated to 2 psia before being pressurized with steam to 3.1 psia. Humidity dwell lasted 1 hr and then the chamber was charged to 23.9 psia with 12/88. Exposure lasted 4 hr. Post-sterilization chamber pressure cycled between 2 psia and 13.9 psia.

[b]The chamber was evacuated to 2 psia before being pressurized with steam to 3.1 psia. Humidity dwell lasted 5 min and then the chamber was charged to 23.9 psia with 12/88. Exposure lasted 5 min. Post-sterilization chamber pressure cycled between 2 psia and 13.9 psia.

[c]The chamber was evacuated to 7 psia before being pressurized with steam to 8 psia. Humidity dwell lasted 1 hr and then the chamber was charged to 32.9 psia with 12/88. Exposure lasted 5 hr. Post-sterilization chamber pressure cycled between 7 psia and 13.5 psia.

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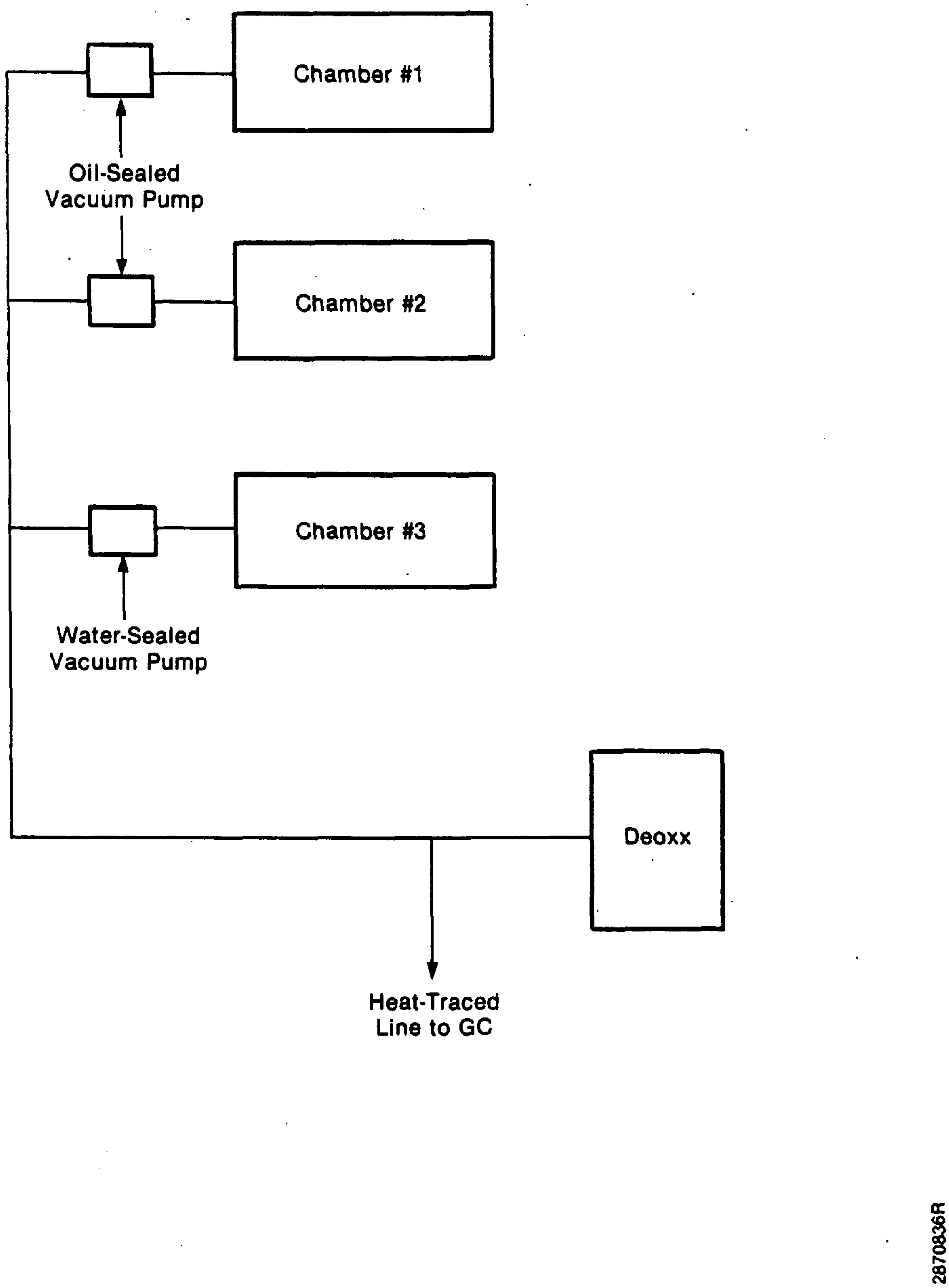

Figure 8. Inlet Sample Location

- a vane anemometer in the center of the duct 26 ft (7.9 m [52 duct diameters]) downstream of the the scrubber outlet and 1.3 ft (40 cm [2.7 duct diameters]) upstream of the first 90 degree (^{o}) bend in the stack addition,
- a 3/16-inch (48-mm) sampling probe,
- two butterfly valves to divert the scrubber exhaust through one of the two parallel ducts,
- two orifice plates in parallel, 6.3 ft (1.9 m [12.7 duct diameters]) downstream of their respective butterfly valves, and 1.3 ft (40 cm [2.7 duct diameters]) upstream of their respective 90^{o} bends, and
- wet and dry bulb temperature probes.

These modifications are diagrammed in Figure 9 and can be seen in the photographs shown in Figures 10-13. Descriptions and operational procedures are contained in the Sampling Procedures Subsection.

SAMPLING PROCEDURES

The semi-continuous direct sampling method was used at both sampling locations. The method is described in detail in Section 4.

Ethylene Oxide Sampling

The EO sampling equipment is shown in Figure 14. Samples were taken simultaneously from both sampling locations using the equipment and procedures described below.

Ethylene Oxide Sampling Equipment--

Sample was withdrawn into heated, 1/4-inch (64-mm), Teflon lines using Teflon-lined diaphragm pumps. A 50-ft (15-m) line was used on the inlet port and a 100-ft (30-m) line was used on the outlet port. Stainless steel, 1/4-inch (64-mm) tees were used prior to the pumps to remove slipstreams from the main sampling lines. The slipstreams were routed through heated, 6-port, gas sampling valves that were used to introduce the samples onto the GC columns. Prior to the 6-port valves were pumps with Teflon-lined diaphragms and stainless steel, 1/4-inch (64-mm), toggle operated shut-off valves. Stainless steel fine metering valves and rotameters were used after the 6-port valves to control the flow rates of the slipstreams. Before

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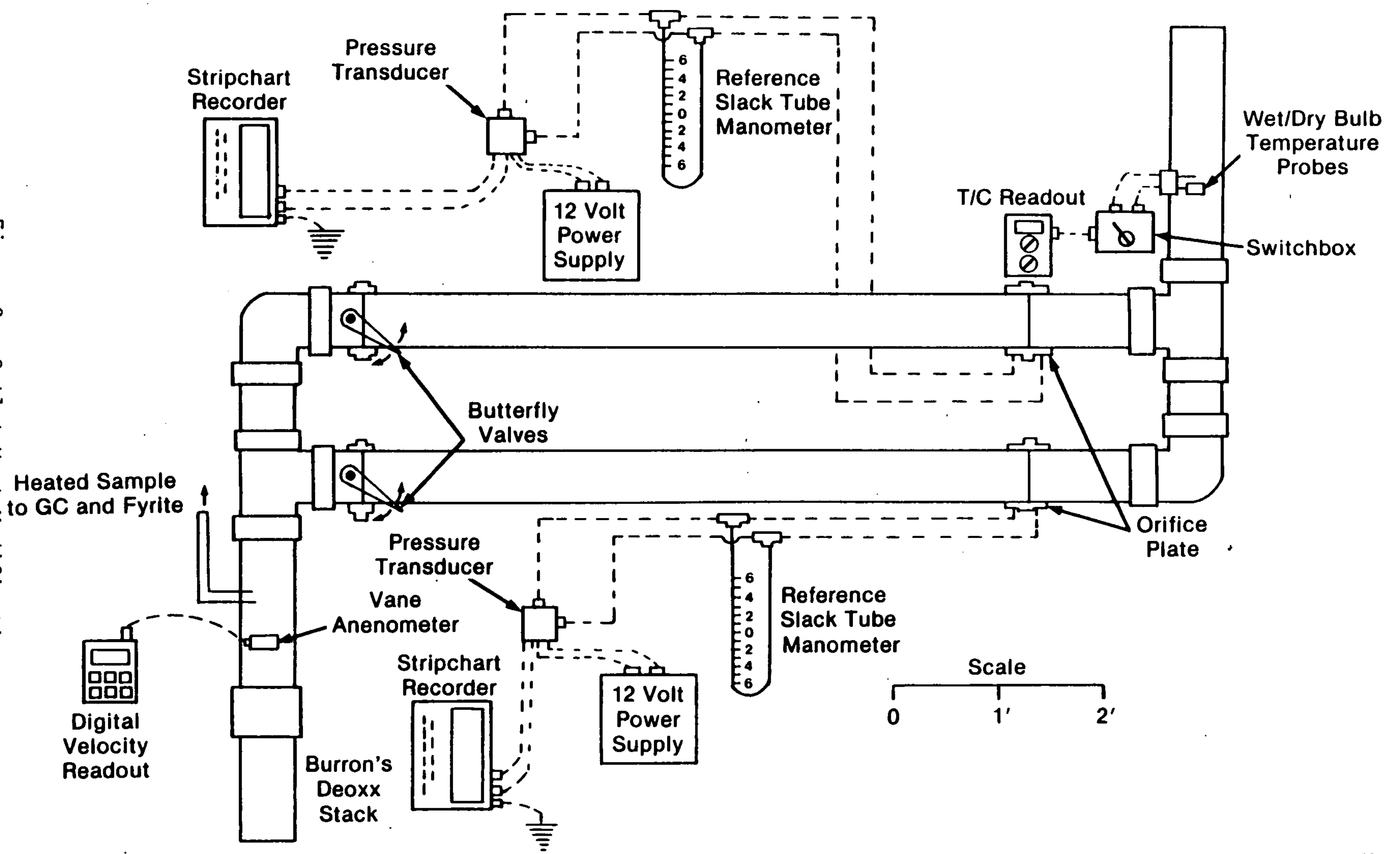

Figure 9. Outlet Vent Modifications

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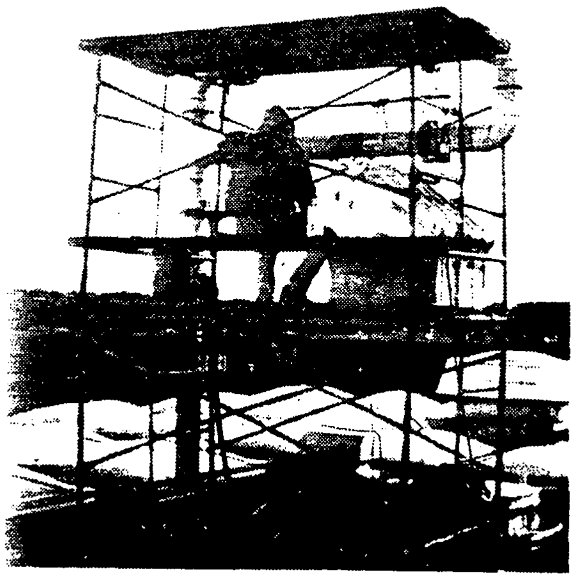

Figure 10. View of Vent Modification From Northeast Side

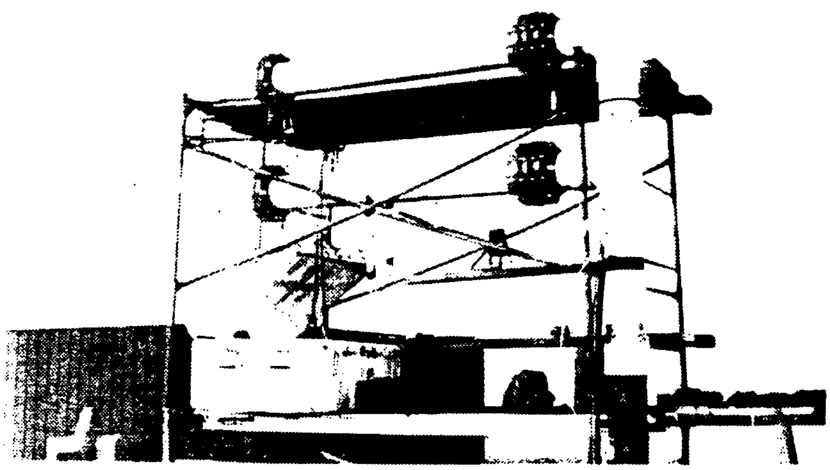

Figure 11. View of Vent Modification From Southwest Side

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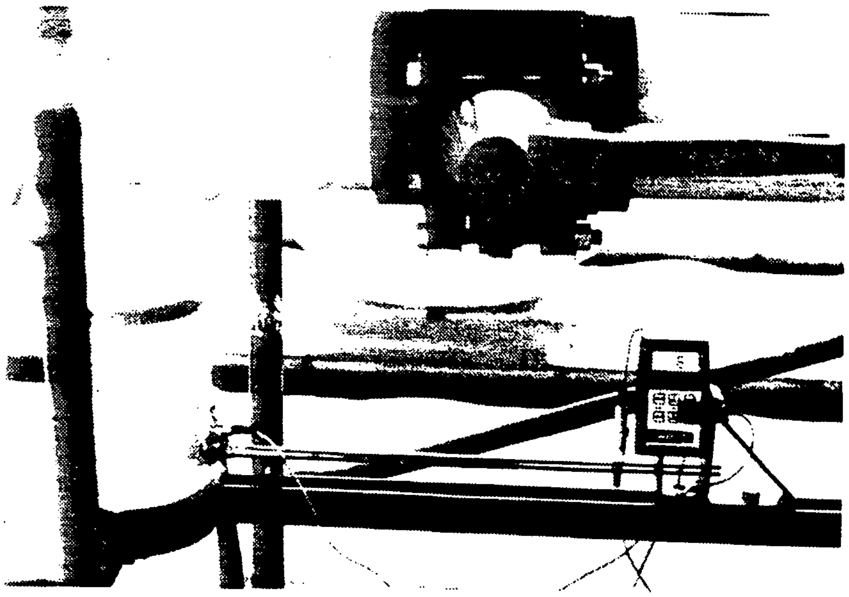

Figure 12. Close-Up of Butterfly Valve and Vane Anemometer Installation

Figure 13. Close-Up of Orifice Flange and Pressure Taps

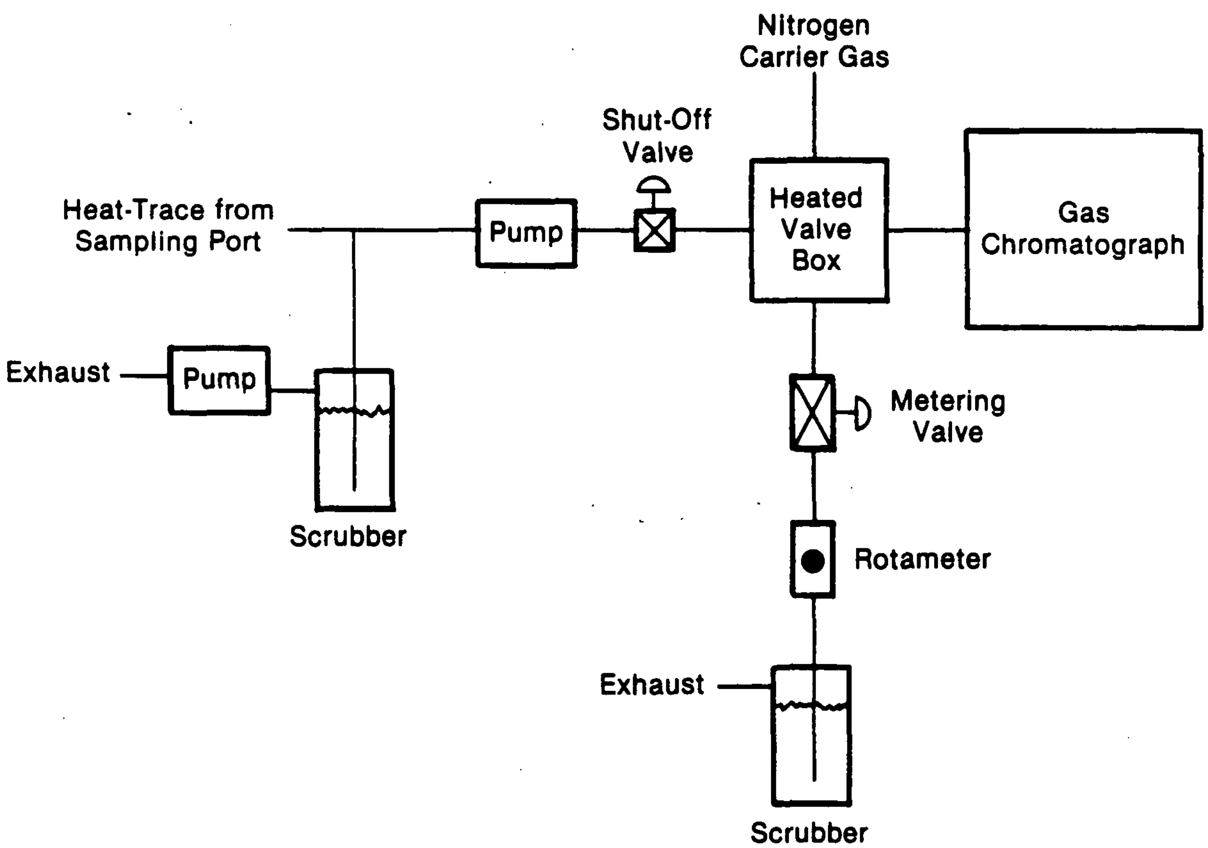

Figure 14. Sampling/Analytical Interface

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exhausting to the atmosphere, the slipstreams and main sample streams were routed through dilute acid (1 N H_2SO_4) scrubbers to remove the EO.

Ethylene Oxide Sampling Operation--

Testing began when the DEOXX scrubber started to exhaust in preparation for the initial chamber evacuation. Each test consisted of seven evacuations, the initial chamber evacuation and pump down and six air in-bleeds and subsequent evacuations. Testing stopped at the start of the seventh air in-bleed. The start time and end time of the evacuations were identified by flow or lack of flow across the orifice plates.

The sampling lines were continually flushed with sample throughout the test day. Flow rates through the slipstreams which flushed the gas sampling loops were maintained at 100 mL/min (0.0035 cfm). Samples were isolated in the 6-port valves by closing the shut-off valves simultaneously. When the rotameters indicated no flow, the sample loops were at atmospheric pressure, and the samples were injected into the GC.

Table 5 compares the EO sampling parameters for each evacuation of each test. For most of the tests, the first sample was acquired at either one, two, three or four minutes after the start of the first evacuation. After the first sample, samples were acquired at three or four minute intervals until the end of the first evacuation. For the second through the seventh evacuations the first sample was acquired at either one, two or three minutes after the start of the evacuation. Again, samples were acquired at three to four minute intervals. The first evacuation was always longer because the initial chamber pressure was higher so a total of five or six samples were acquired during the first evacuation. For the second through seventh evacuations, a total of three or four samples were acquired during each evacuation. In test 13, the chamber was not evacuated to as low a pressure as in the other tests, so only four samples were acquired during the first evacuation and one sample during each of the subsequent six evacuations.

Volumetric Flow Rate Measurement

Volumetric flow rate measurements of scrubber exhaust were performed at the scrubber outlet location. A vane anemometer followed by two orifice plates in parallel was used to measure velocity. Two orifice plates were used to cover the range of expected flow rates and composition of the vent

TABLE 5. COMPARISON OF ETHYLENE OXIDE SAMPLING OPERATION PARAMETERS WITH TEST CONDITIONS

	Test 6-12,14,15		Test 13	
	Evacuation		Evacuation	
Parameter	1	2-7	1	2-7
Time from start of evacuation to first sample	1,2,3 or 4 minutes	1,2, or 3 minutes	3 minutes	3 or 4 minutes
Sampling Interval	3 or 4 minutes	3 or 4 minutes	4 or 5 minutes	
Total Samples Acquired	5 or 6	3 or 4	4	1
Chamber Pressure				
at start of evac.	23 psia	13.9 psia	33 psia	13.9 psia
at end of evac.	2 psia	2 psia	7.5 psia	7.5 psia

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gas. Temperatures were measured using a bimetallic temperature probe and a pyrometer.

Vane Anemometer--

A PACER INDUSTRIES Model AD4000 vane anemometer was used to measure exhaust flows of <300 feet per minute (ft/min [90 m/min]). The vane anemometer probe head is factory calibrated using a Laser anemometer as reference in a 6-inch (15-cm) diameter wind tunnel. The reference calibration, performed in air, is contained in an internal microprocessor chip. Placement of the anemometer was upstream of the orifice plates as shown in Figure 9. A close-up of the vane anemometer placement in the stack extension is shown in Figure 12. Linear velocities were recorded manually every 2 min.

Orifice Plates--

Two standard, squared-edged orifice plates with standard pipe taps were mounted in parallel ducts as shown in Figures 9-11 to allow the determination of scrubber exhaust flow rate. The orifice diameters used were 1.763-inch (4.48-cm) and 2.591-inch (6.58-cm). The 1.763-inch (4.48-cm) diameter orifice plate was used to ensure accurate velocity head measurement during the latter part of the evacuations and when the low molecular weight of the vent stream resulted in velocities as low as 300 ft/min (90 m/min). The 2.591-inch (6.58-cm) diameter orifice was used during the initial portion of the evacuations and when the high molecular weight of the vent stream resulted in velocities approaching 1000 ft/min (300 m/min). Butterfly valves, as shown in Figure 12, were used to isolate the two orifice plates. The standard pressure taps on the orifice flanges were connected to Setra pressure transducers that were calibrated from 0-10 inches of water (inches H_2O [0-254 kg/m^2]). Output from the pressure transducers was recorded on stripchart recorders. A close-up of the orifice flanges and pressure taps is shown in Figure 13.

Stack Temperature--

Exit gas temperatures were measured at the scrubber outlet location. A bimetallic temperature sensor was placed in the duct as shown in Figure 9. Stack temperatures were digitized by a calibrated pyrometer and recorded every 2 min.

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Sampling Operation--

The two parallel orifice plates in series with the vane anemometer were used to measure velocity. As previously mentioned, vane anemometer and stack temperature readings were recorded every 2 min during the initial exhaust and subsequent air wash periods. The differential pressure measurement from the orifice plates was continuously recorded with stripchart recorders.

The initial sterilizer exhaust velocity was determined using the large (2.591-inch [6.58 cm] diameter) orifice through the depressurization and most of the pump down phase. When the flow registered less than 3 inches H_2O (76 kg/m^2) of differential pressure for the large orifice, the flow was diverted through the smaller (1.763-inches [4.48-cm]) diameter orifice. Figure 15 shows an example of the differential pressures measured using the large orifice during a typical initial exhaust.

Velocity measurements taken during the second to seventh evacuations used the same orifice plate procedures. Due to the reduced molecular weight of the exhaust gas during these evacuations, the duration of flow requiring use of the larger diameter orifice was usually shorter. However, during the second evacuation some of the heavier molecular weight gas from the first evacuation remained in the system. The exhaust of this heavier molecular weight gas lengthened the time the larger orifice plate was used to measure the pressure differential. Similarly, the first few minutes of the first evacuation contained gas from a previous evacuation.

Moisture Determination

The percent moisture of the stack gas was determined by the wet bulb/dry bulb method. The procedure measured relative humidity which was converted to percent moisture. Wet and dry bulb temperature measurements used to determine relative humidity were recorded at least once during each exhaust episode.

Molecular Weight Determination

The molecular weight of the exhaust stream, which changed with time due to EO removal, was needed to calculate the flow rate. Nitrogen, oxygen, carbon dioxide, water, EO, and CFC-12 were considered the main components of the sterilizer exhaust gas. The emissions of EO and CFC-12 were continuously

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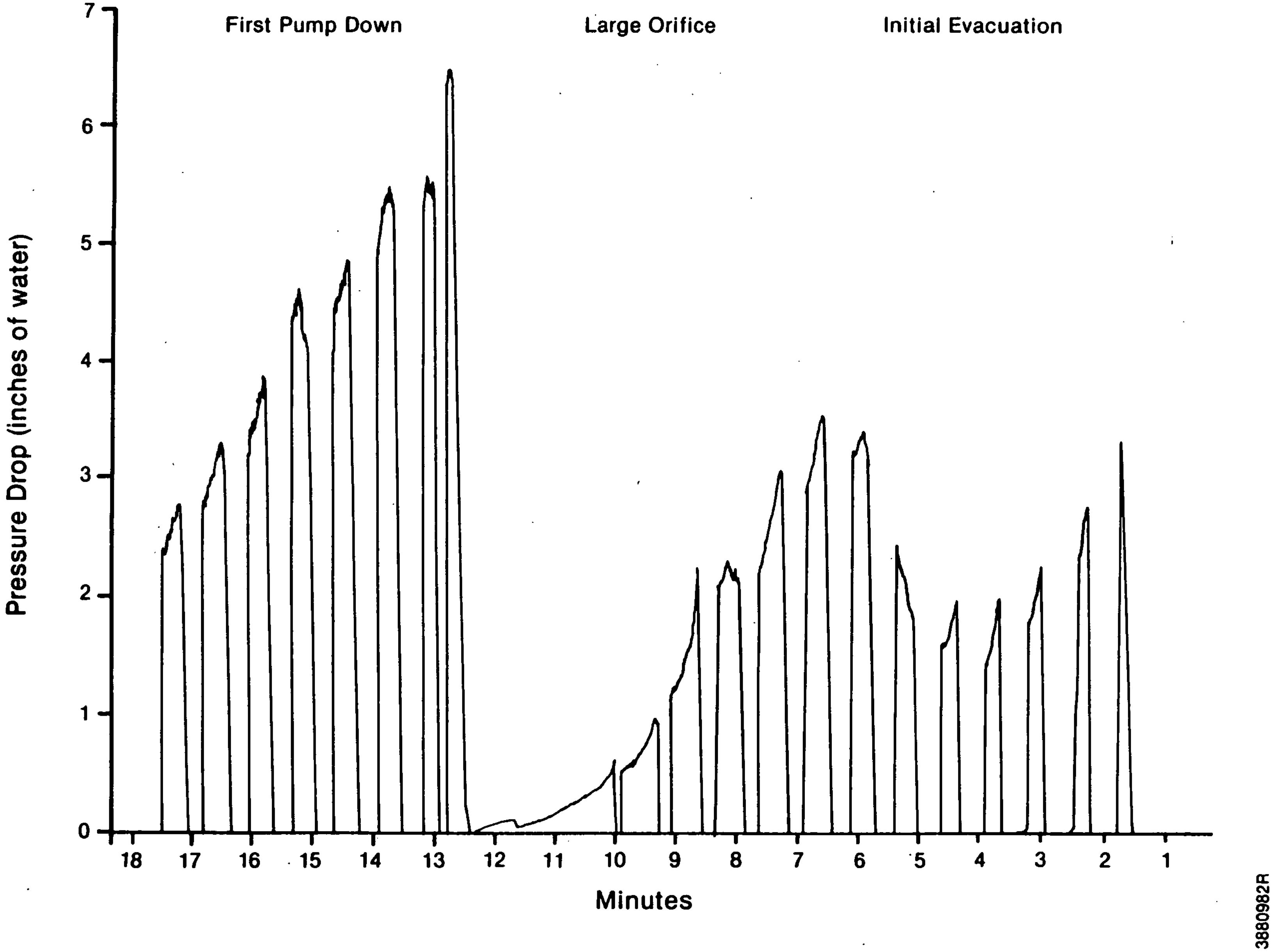

Figure 15. Measured Differential Pressures During First Evacuation

monitored by GC/FID. Emissions of oxygen and carbon dioxide were measured with Fyrite oxygen and carbon dioxide indicators. The nitrogen concentration was determined by difference.

Fyrite Oxygen And Carbon Dioxide Indicators--

BACHARACH Fyrite oxygen and carbon dioxide indicators were used to determine percent levels of oxygen and carbon dioxide in the sterilizer exhaust at the outlet sampling location. Fyrite indicators use volumetric displacement involving chemical absorption of oxygen or carbon dioxide from the sample. The reagent used to absorb carbon dioxide was potassium hydroxide, and chromous chloride was the absorbent for oxygen. Accuracy of analysis was $\pm 0.5\%$.

Sampling Operation--

Percent levels of oxygen and carbon dioxide were usually measured once during each evacuation. For several of the runs oxygen was measured at 1- or 2-min intervals. These measurements were used to determine the dead volume of the scrubber system. Measurements of carbon dioxide in the exhausts were numerically negative, indicating an interference with the potassium hydroxide absorption solution. Because carbon dioxide levels were expected to be low (<1% [v]) an alternate method of determining carbon dioxide was not pursued. Sample was removed from the stack downstream of the vane anemometer. An aspirator bulb was used to pull the sample from the stack.

ANALYTICAL PROCEDURES

The analytical method used for the measurement of the EO and CFC-12 was gas chromatography with flame ionization detection (GC/FID). The CFC-12 concentration was needed for the determination of the gas stream molecular weight. The equipment and procedures used are described below.

Analytical Equipment Description

Some of the analytical equipment was shown in Figure 14. The dual FID Varian 3400 GC was equipped with a Nutech heated valve box containing two 6-port valves. An 0.25 mL loop was used on the inlet sample line and a loop of 2 mL was used on the outlet sample line. The analytical columns were 10 ft (3 m) x 1/8 inch (3 mm) O.D. stainless steel columns containing 5% Fluorcol on 60/80 Carbopack B. The FID electrometers were connected to Shimadzu CR1-A integrators.

Operating Conditions

The GC column oven was operated isothermally at 100^{o}C, the injector oven at 175^{o}C, and the detector oven at 200^{o}C. Nitrogen carrier gas flow rates were 30 mL/min on the outlet channel and 60 mL/min on the inlet channel. The FID support gas flow rates recommended by the GC manufacturer were used.

The same FID electrometer range was used for the EO and CFC-12 on the inlet channel but the range used varied from 10^{-9} to 10^{-11} depending on the inlet sample concentration. The FID electrometer range was programmed on the outlet channel. A range of 10^{-10} to 10^{-12} was used for the EO and 10^{-8} to 10^{-10} was used for the CFC-12. The electrometer range was programmed to switch at 1.1 min during the first evacuations and at 1.55 min during the second through seventh evacuations.

Analytical Sampling Procedures

The sample loops were purged with sample flowing at 100 mL/min for a minimum of 20 s. Samples were taken simultaneously at the inlet and at the outlet by closing toggle valves in-line previous to the sample loops. The pressure in the loops was allowed to equilibrate to atmospheric pressure, as indicated by lack of flow through the rotameters, before the injections were made. Data collection on the inlet channel was stopped after the elution of the CFC-12 peak. On the outlet channel, although the last peak did not elute until after 3 min, data collection was stopped after about 2.5 min to allow the integrator time to print out its report before the next injection.

The first sample was injected from 1-4 min after the start of the initial exhaust and additional samples at 3-4 min thereafter. For subsequent exhausts, sampling was started 1-3 min after the first indication of flow through the stack. Five to six samples were acquired during the first evacuation and three to four during the subsequent evacuations except during Test 13 when four samples were acquired during the initial evacuation and one sample during the subsequent evacuations.

Gas Chromatograph Calibration

Both channels of the chromatograph were calibrated for EO and CFC-12 at the beginning and end of the day. At least one standard was also analyzed between tests. Standards were purchased from Scott Specialty Gases, Scientific Gas Products, and MG Industries and ranged in EO concentration from less than 1 ppmv to 20% (v) and in CFC-12 concentration from 1200 ppmv to 62.5% (v). In addition, lecture bottles containing 99.9% EO and CFC-12 were used to verify response at the upper levels of concentrations observed in the vent streams. Calibration curves consisted of a minimum of three standards which bracketed the sample concentrations.

CALCULATIONS

The data were reduced using LOTUS® 1-2-3 software. Rounding was performed at the completion of the calculations.

Ethylene Oxide and CFC-12 Concentration

Calibration curves were prepared by taking the logarithm of the peak area and plotting that logarithm versus the logarithm of the concentration. Although the use of logarithm-logarithm plots is a departure from normal practice, the logarithm procedure weighted each point of the calibration curve more equally than the use of a straight calibration curve. Equal weighting was important because the calibration curve covered six orders of magnitude. Under those conditions, the highest standard (100% [v]) received the greatest weight when using a straight response versus concentration curve. Essentially, the highest standard by being so much larger than the other standards determined the calibration curve. Unfortunately, the highest standard was also the standard most likely to be inaccurate due to possible curvature in the response curve at high concentrations and irregularites in response due to possible column overloading. With a logarithm-logarithm plot the high point that was most likely to be in error received less weight and the middle points that were most likely to be correct received more weight. Table 6 shows a comparison of data calculated using the logarithm calibration to data calculated using a standard curve.

The slope (M) and the y-intercept (B) were obtained from the least squares fit of the data points to the curve using Equations 7 and 8:

$$M=[n(\Sigma XY) - (\Sigma X)(\Sigma Y)/[n(\Sigma X^2) - (\Sigma X)^2] \quad \text{(Equation 7)}$$

$$B = (\Sigma Y)/n - M(\Sigma X)/n \quad \text{(Equation 8)}$$

where n is the number of standard concentrations used, X is the logarithm of the standard concentration, and Y is the logarithm of the peak area.

The calibration curves are shown in Figures 16-19. The EO inlet calibration curve is shown in Figure 16, the CFC-12 inlet calibration curve

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TABLE 6. COMPARISON OF ETHYLENE OXIDE CONCENTRATIONS CALCULATED USING LOGARITHM-LOGARITHM AND STANDARD CALIBRATION CURVES FOR DATA FROM THE SCRUBBER OUTLET DURING TEST 14

Elapsed Time (min)	Concentration in ppmv	
	Logarithm Method[a]	Standard Method[b]
5	17.69	19.52
8	35.52	37.36
12	57.43	59.12
16	59.21	60.87
20	63.49	65.11
24	61.89	63.53
44	20.90	22.74
48	56.78	58.47
52	41.58	43.39
71	32.69	34.54
75	30.07	31.92
79	33.05	34.89
97	17.05	18.88
101	15.58	17.39
105	10.93	12.70
124	9.28	11.03
128	6.54	8.24
132	7.36	9.08
150	5.49	7.17
154	4.41	6.06
158	2.47	4.07
177	2.11	3.70
181	2.35	3.94
185	3.60	5.23

[a] Calibration from 1 ppmv to 12.5% (v).

[b] Calibration from 1 ppmv to 502.4 ppmv.

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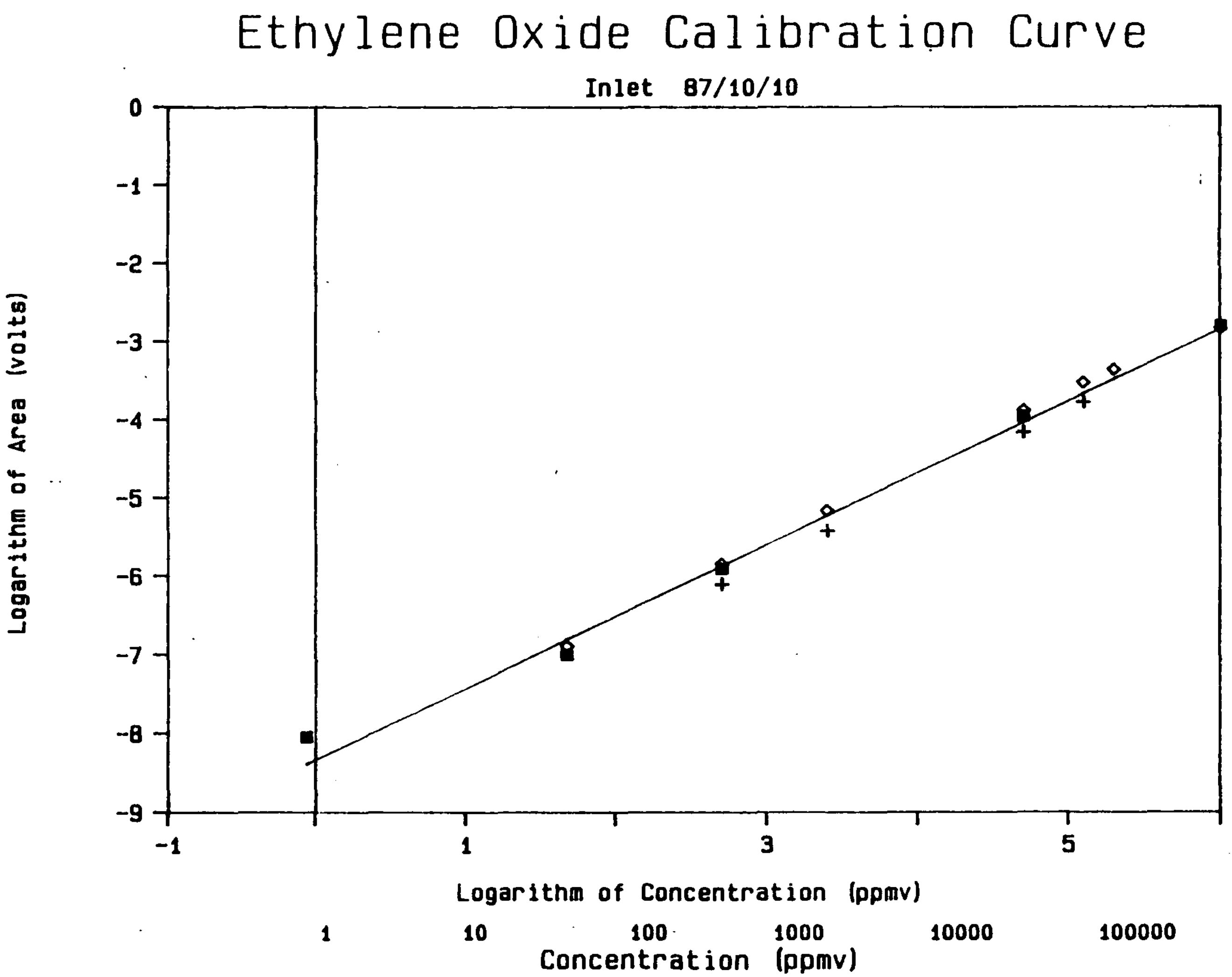

Figure 16. Ethylene Oxide Calibration Curve Used for Quantitation of Scrubber Inlet Samples

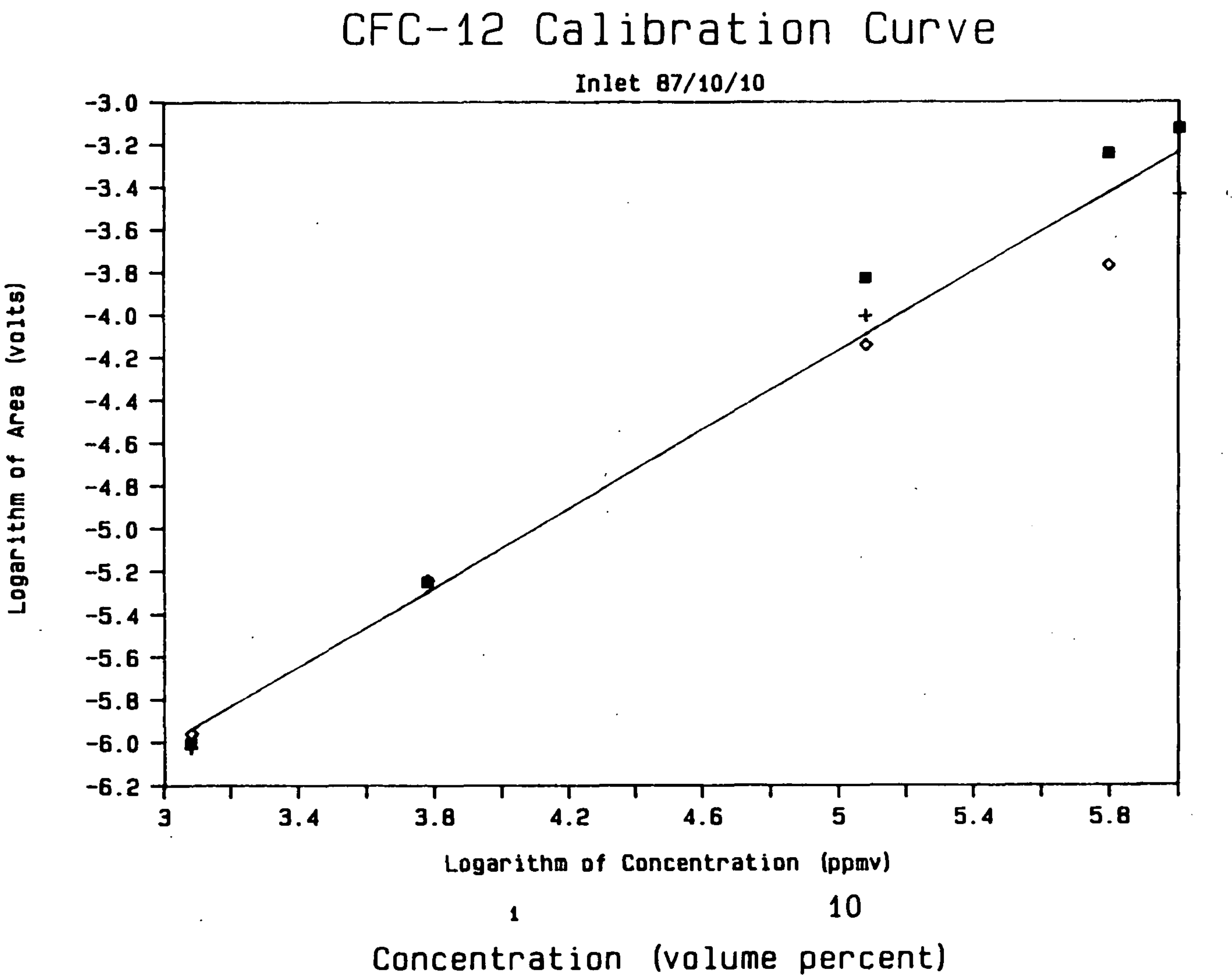

Figure 17. Chlorofluorocarbon-12 Calibration Curve Used for Quantitation of Scrubber Inlet Samples

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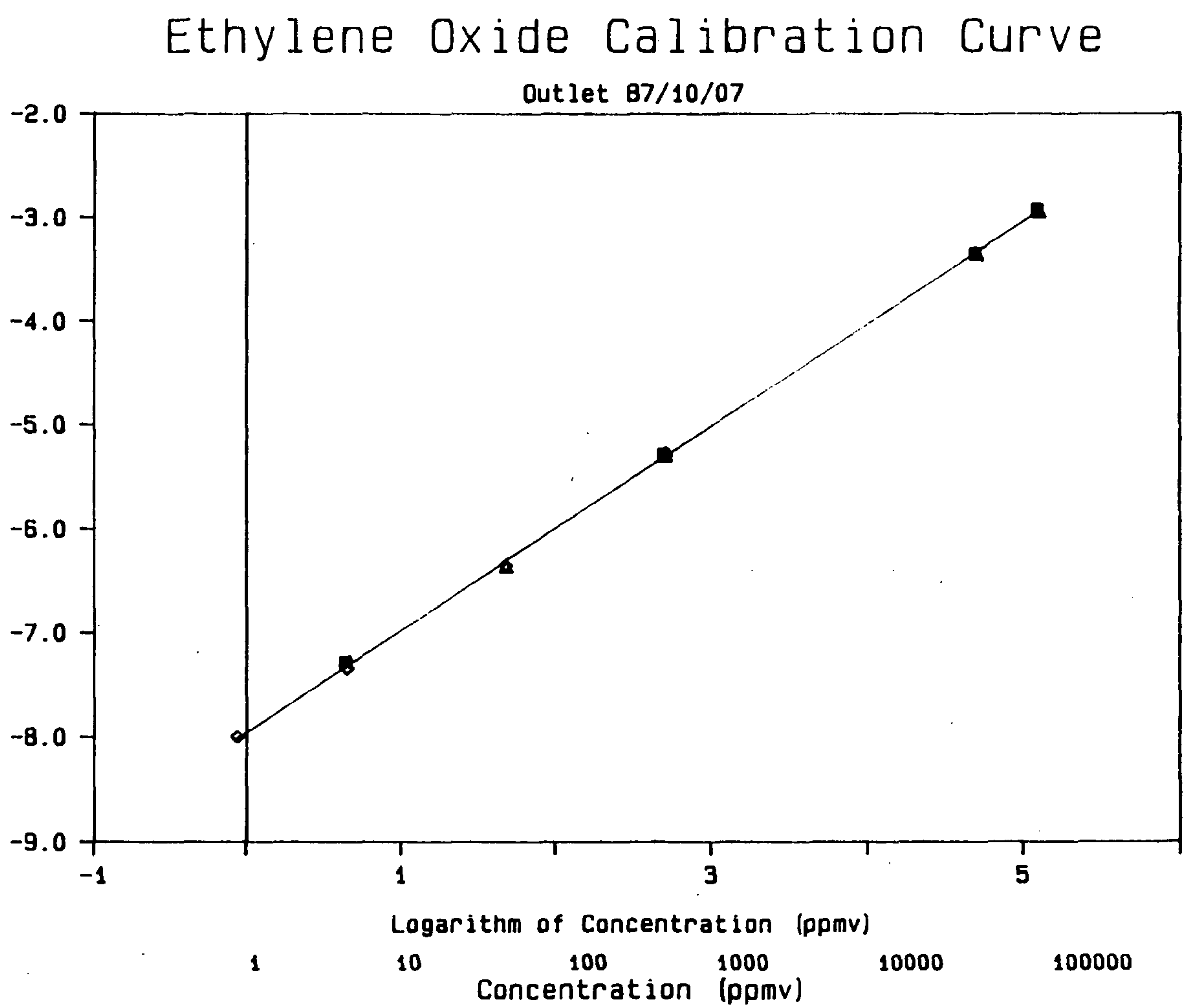

Figure 18. Ethylene Oxide Calibration Curve Used for Quantitation of Scrubber Outlet Samples

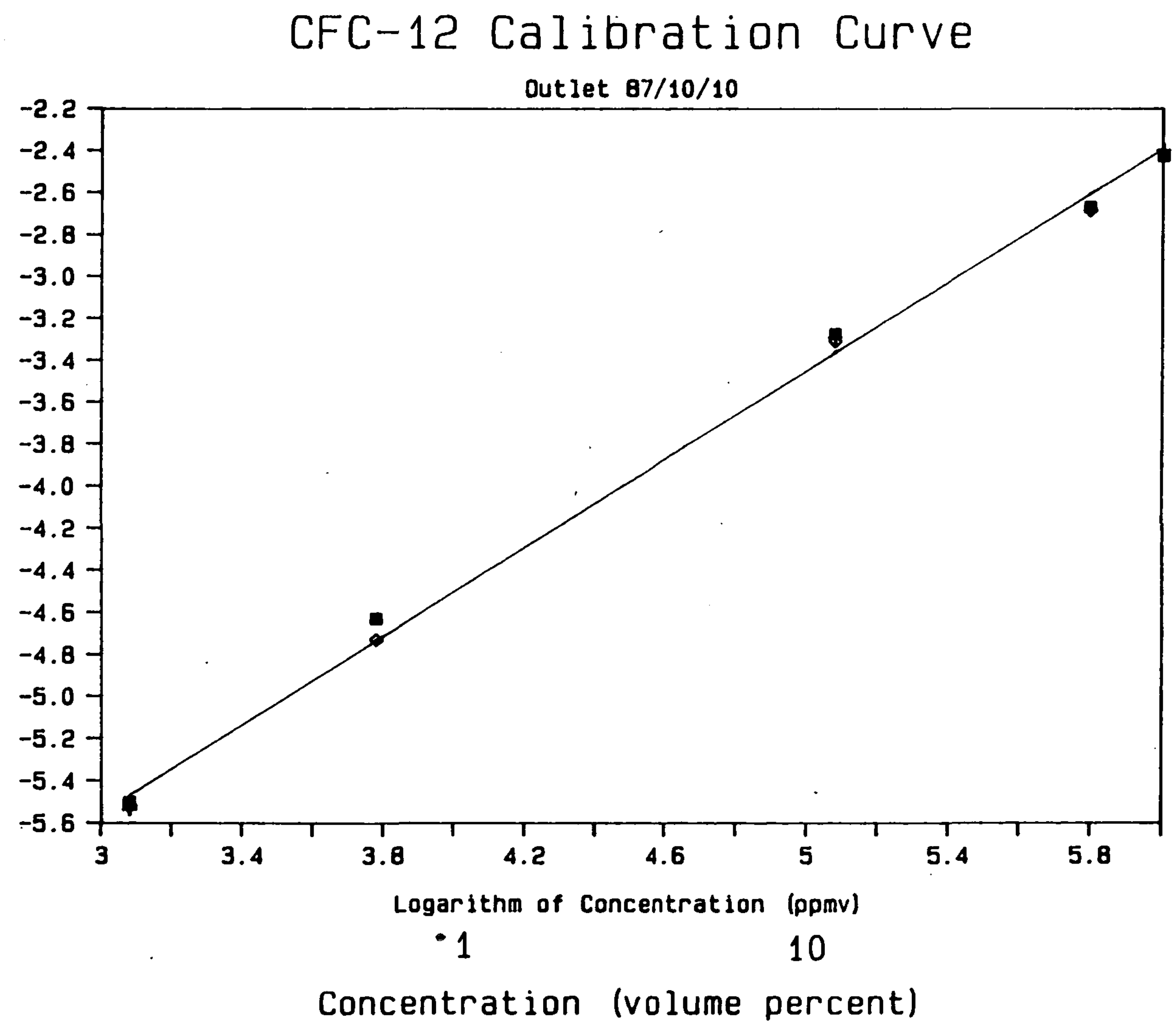

Figure 19. Chlorofluorocarbon-12 Calibration Curve Used for Quantitation of Scrubber Outlet Samples

in Figure 17, the EO outlet calibration curve in Figure 18, and the CFC-12 outlet calibration curve in Figure 19. Many of the standards were injected several times during the day as indicated by the various symbols on the graphs. The lines represent the least squares best fit using all of the data points. In general, for the inlet analyses the system was calibrated from 1 ppmv to 100% (v) for EO and from 500 ppmv to 100% (v) CFC-12 and for the outlet analyses from 1 ppmv to 12.5% (v) for EO and from 500 ppmv to 100% (v) for CFC-12.

As shown in Figures 20 and 21, at the scrubber outlet the EO and CFC-12 concentrations were interpolated at 10-sec intervals for the first evacuations. Usually, the concentrations were assumed to increase linearly, plateauing at a maximum determined by an average of the data points after the concentration versus time curve leveled off. In some cases the concentration was assumed to decrease linearly after reaching a maximum and in other cases the concentration was assumed to be constant throughout the evacuation.

For the second evacuations the concentrations were assumed to decrease linearly where enough data were present to validate that assumption. In most cases an average concentration was used. Examples of the concentration interpolations for the second evacuations are shown in Figures 22 and 23. In all cases for the third through seventh evacuations average concentrations were used.

At the scrubber inlet the EO and CFC-12 concentrations were interpolated at two-minute intervals for the first evacuations as shown in Figures 24 and 25. The same interpolation procedures were used at the scrubber inlet as at the scrubber outlet. Examples of the concentration interpolations at the scrubber inlet for the second evacuations are shown in Figures 26 and 27.

Vent Stream Molecular Weight

The molecular weight of the vent stream (MW_{vs}) is the sum of the molecular weight (MW) of each component multiplied by the mole fraction (C) of that component in the vent stream:

$$MW_{vs} = C_a MW_a + C_b MW_b + \ldots + C_z MW_z \qquad \text{(Equation 9)}$$

The components in the vent stream that were considered to contribute to the molecular weight were EO, CFC-12, oxygen, nitrogen, and water. Carbon dioxide was not included because it was present at low levels (<1 volume percent).

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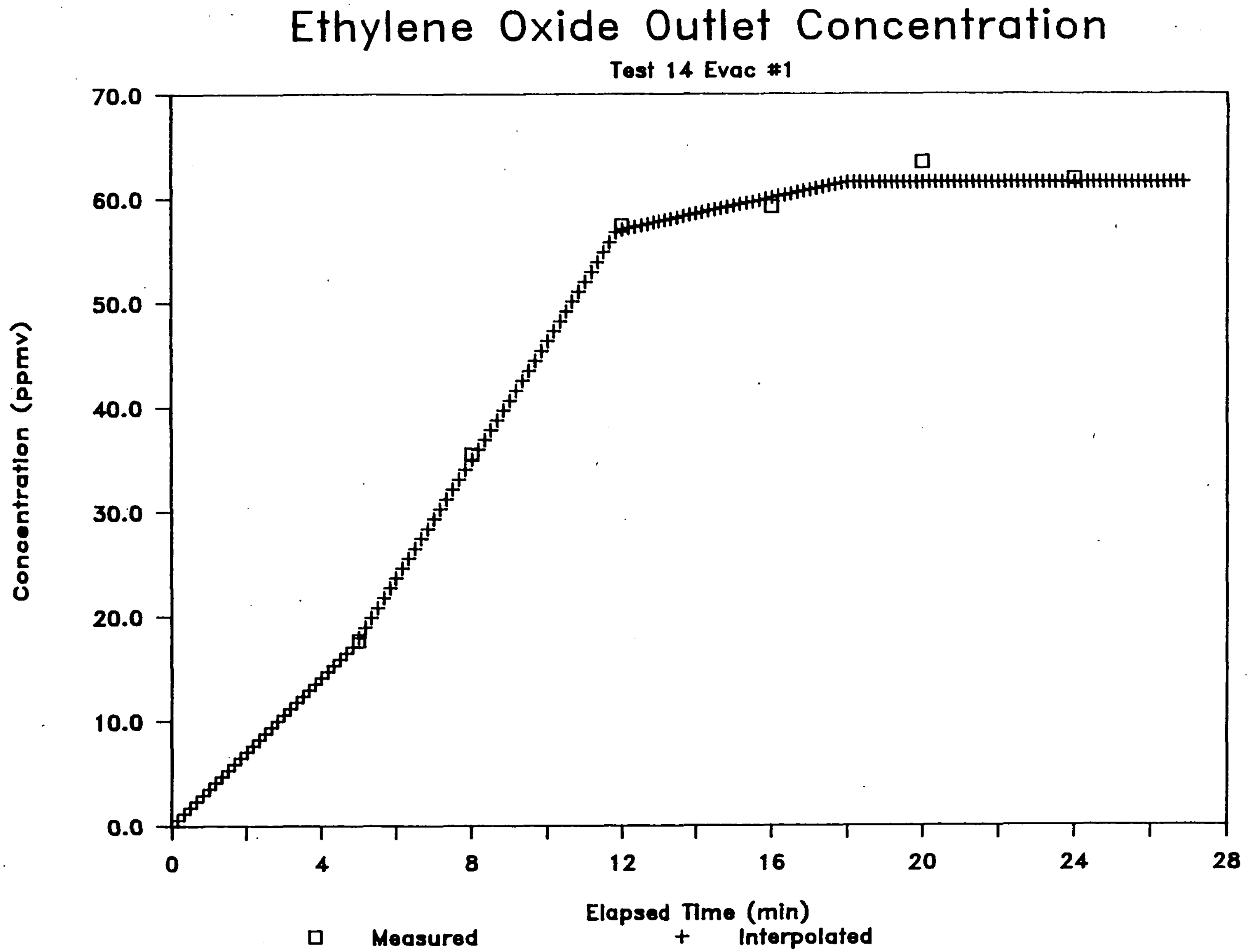

Figure 20. Interpolated EO Scrubber Outlet Concentrations for for Test 14 Evacuation 1

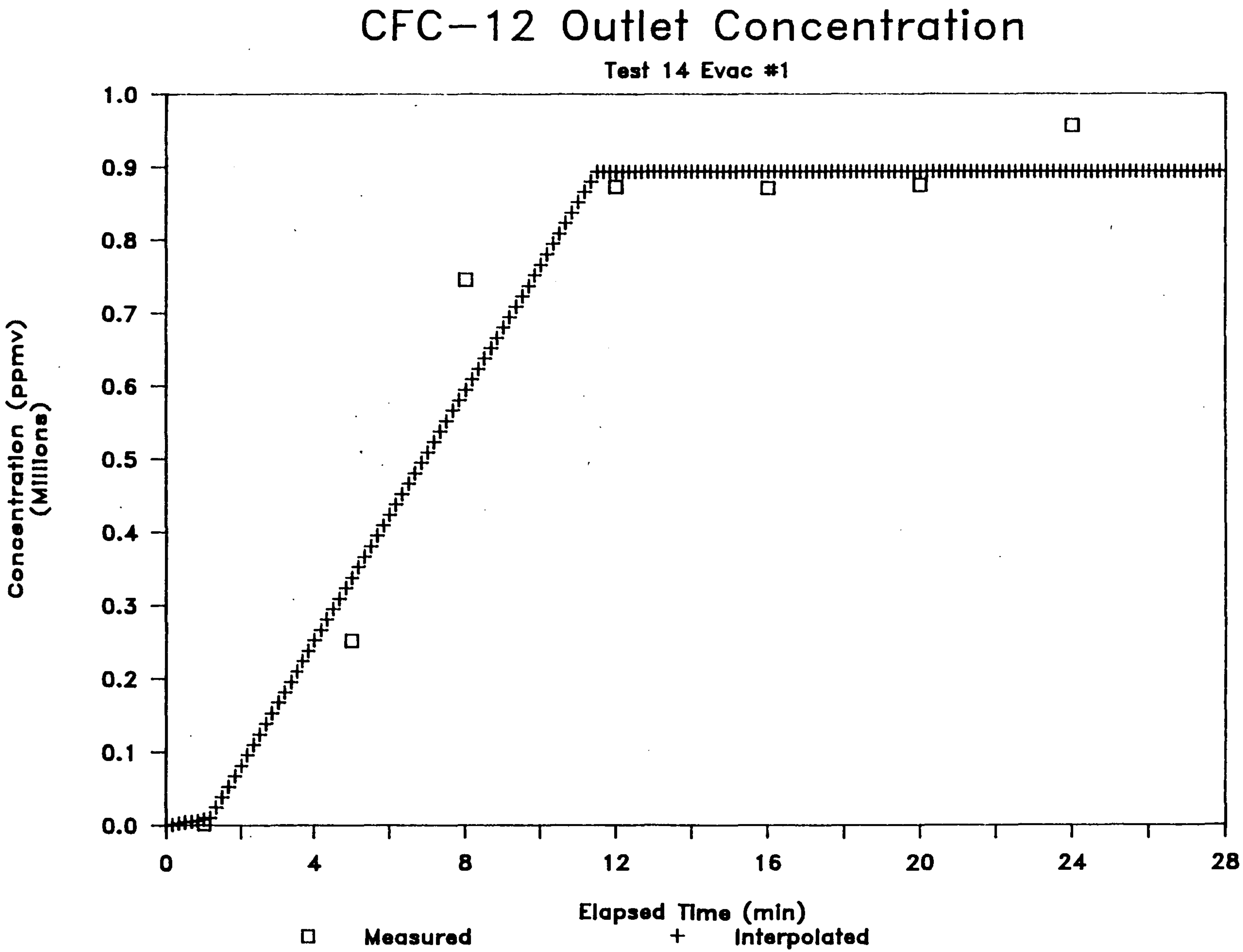

Figure 21. Interpolated CFC-12 Scrubber Outlet Concentrations for Test 14 Evacuation 2

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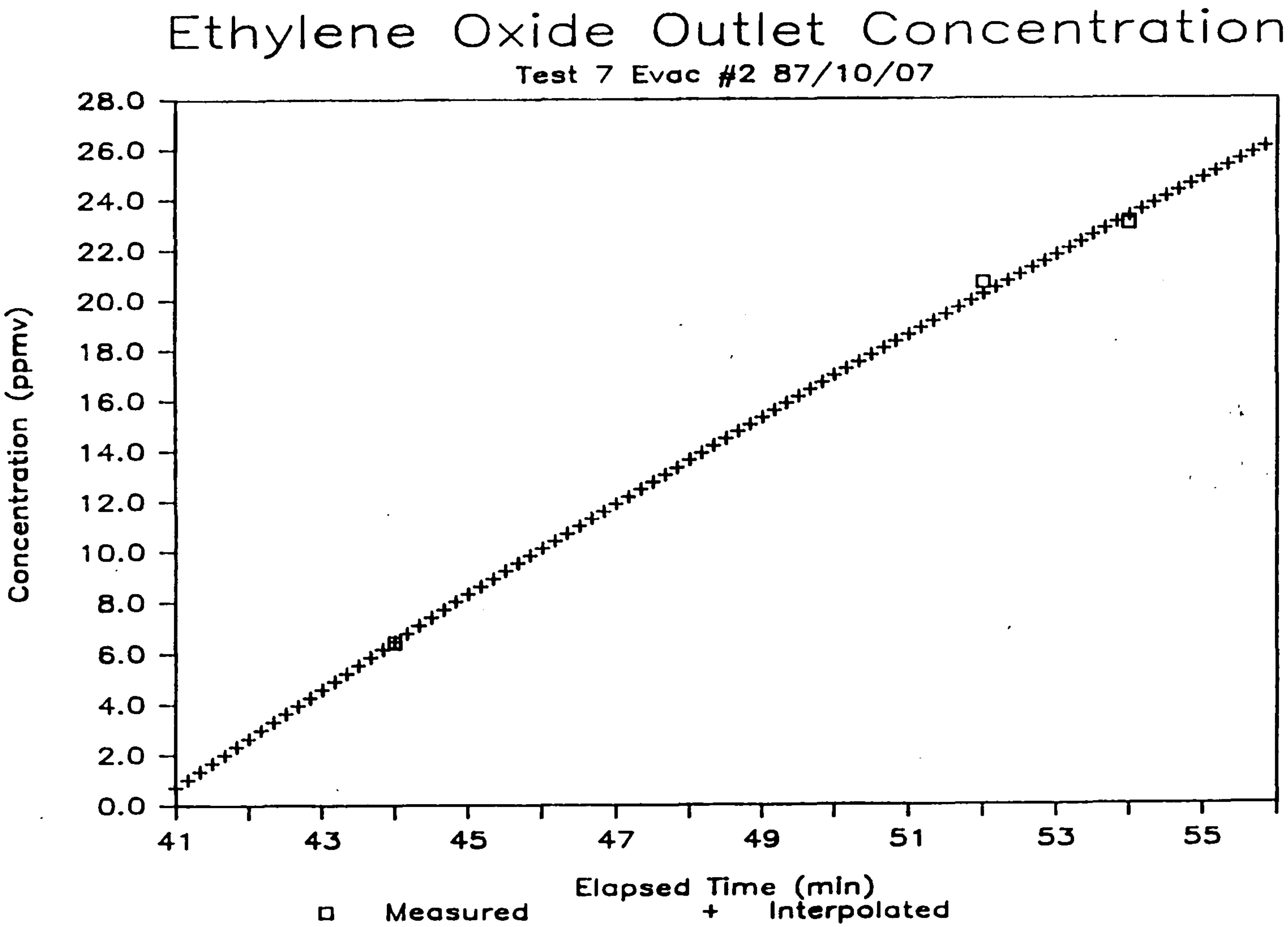

Figure 22. Interpolated EO Scrubber Outlet Concentrations for Test 7 Evacuation 2.

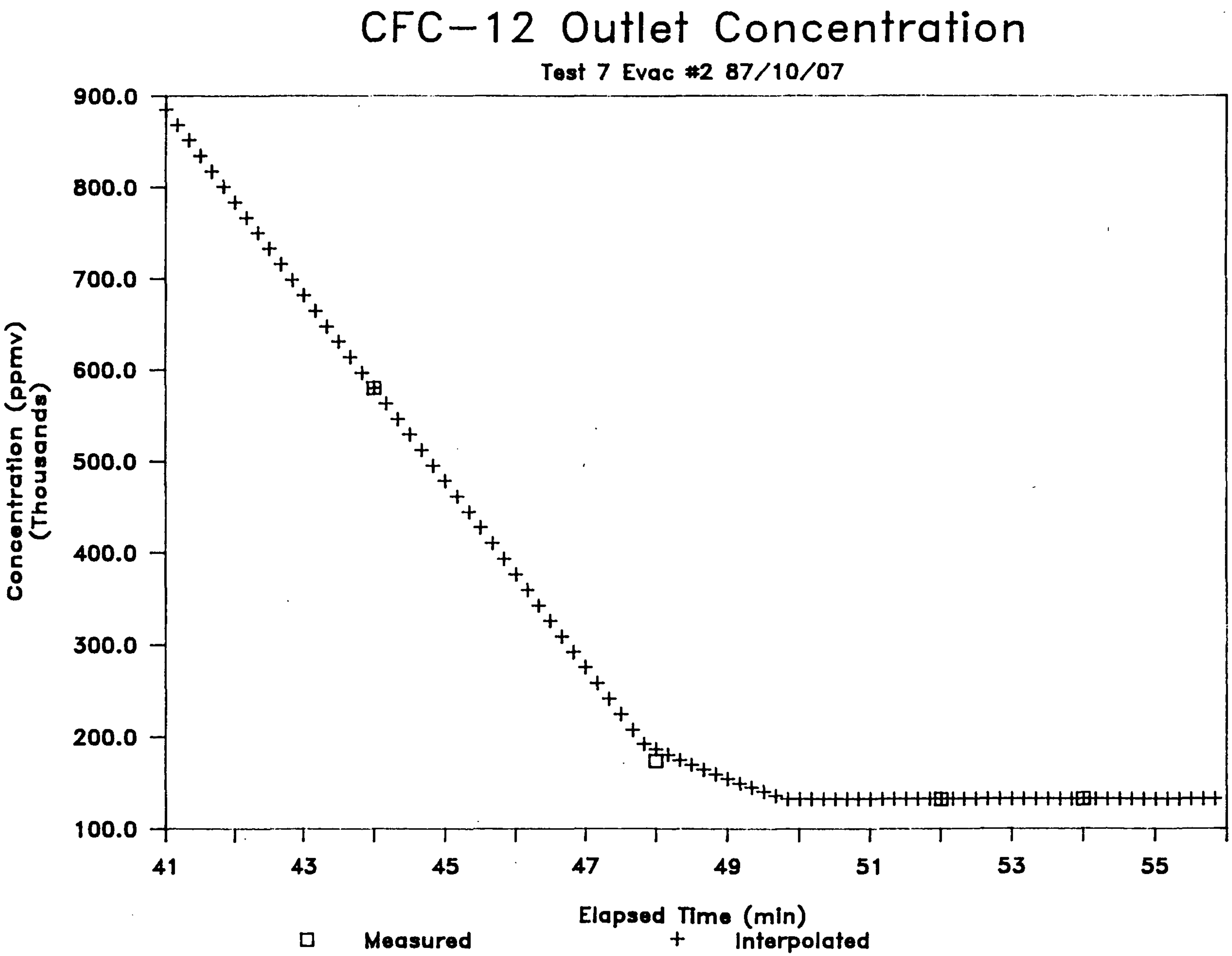

Figure 23. Interpolated CFC-12 Scrubber Outlet Concentrations for Test 7 Evacuation 2

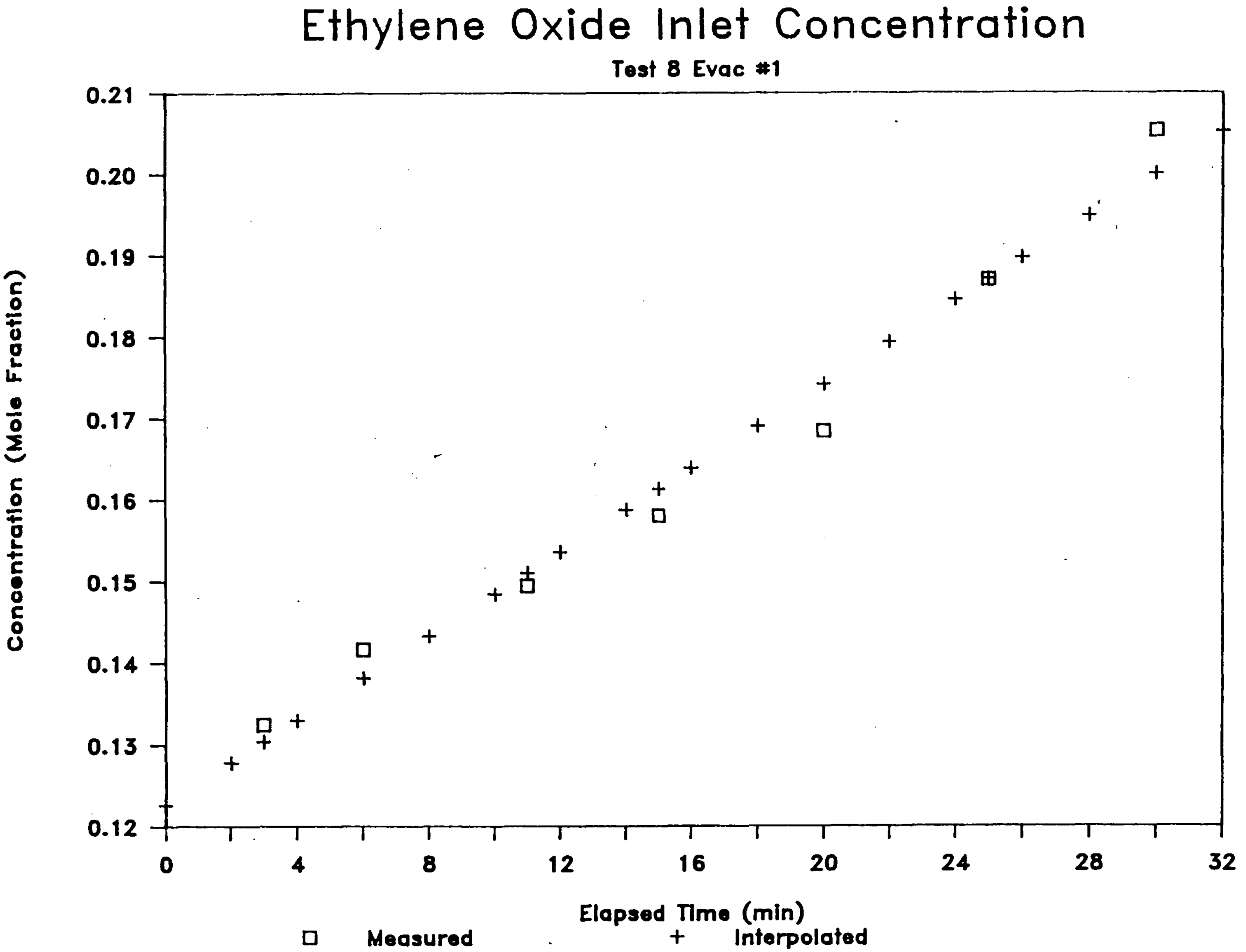

Figure 24. Interpolated EO Scrubber Inlet Concentrations for Test 8 Evacuation 1

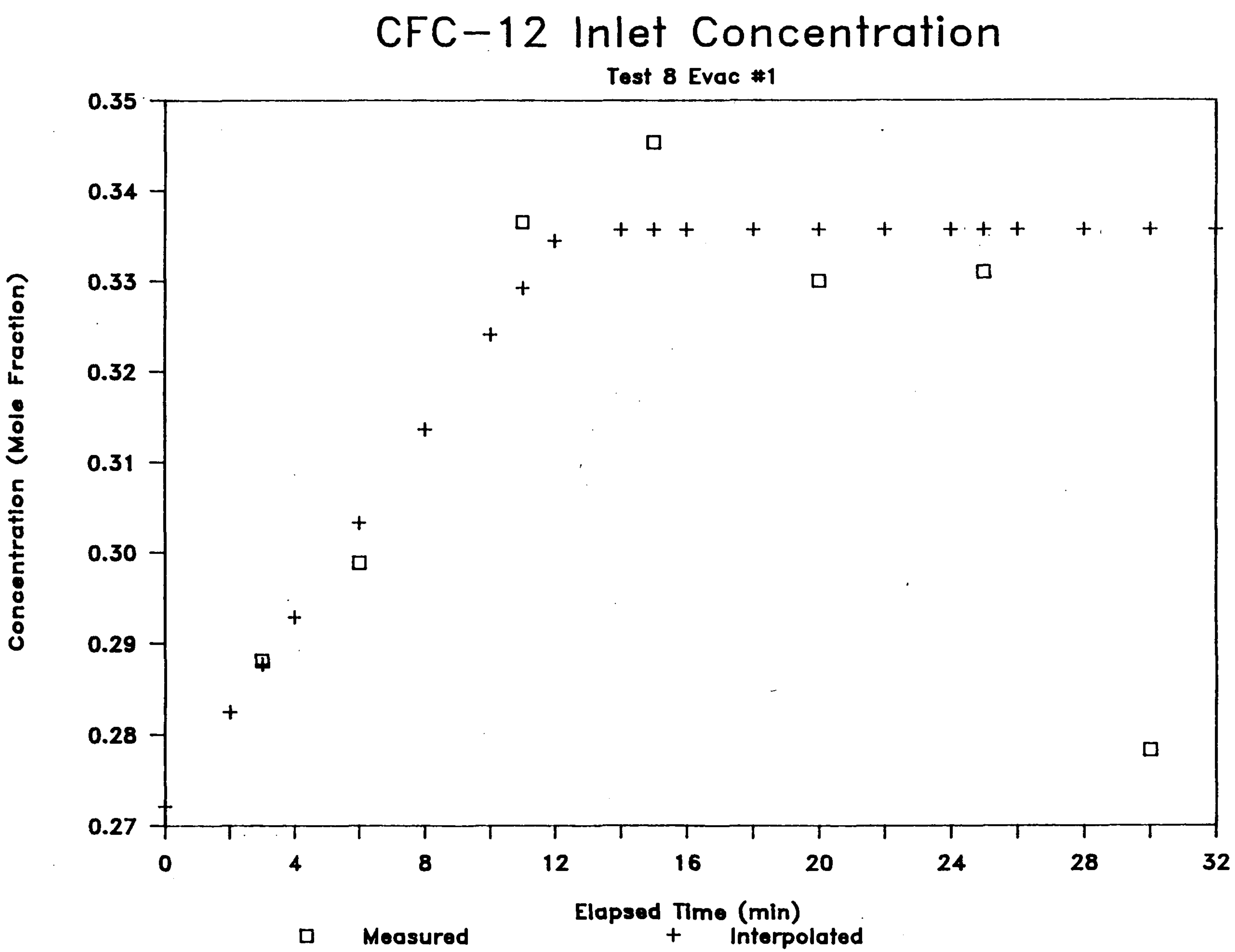

Figure 25. Interpolated CFC-12 Scrubber Inlet Concentrations for Test 8 Evacuation 1

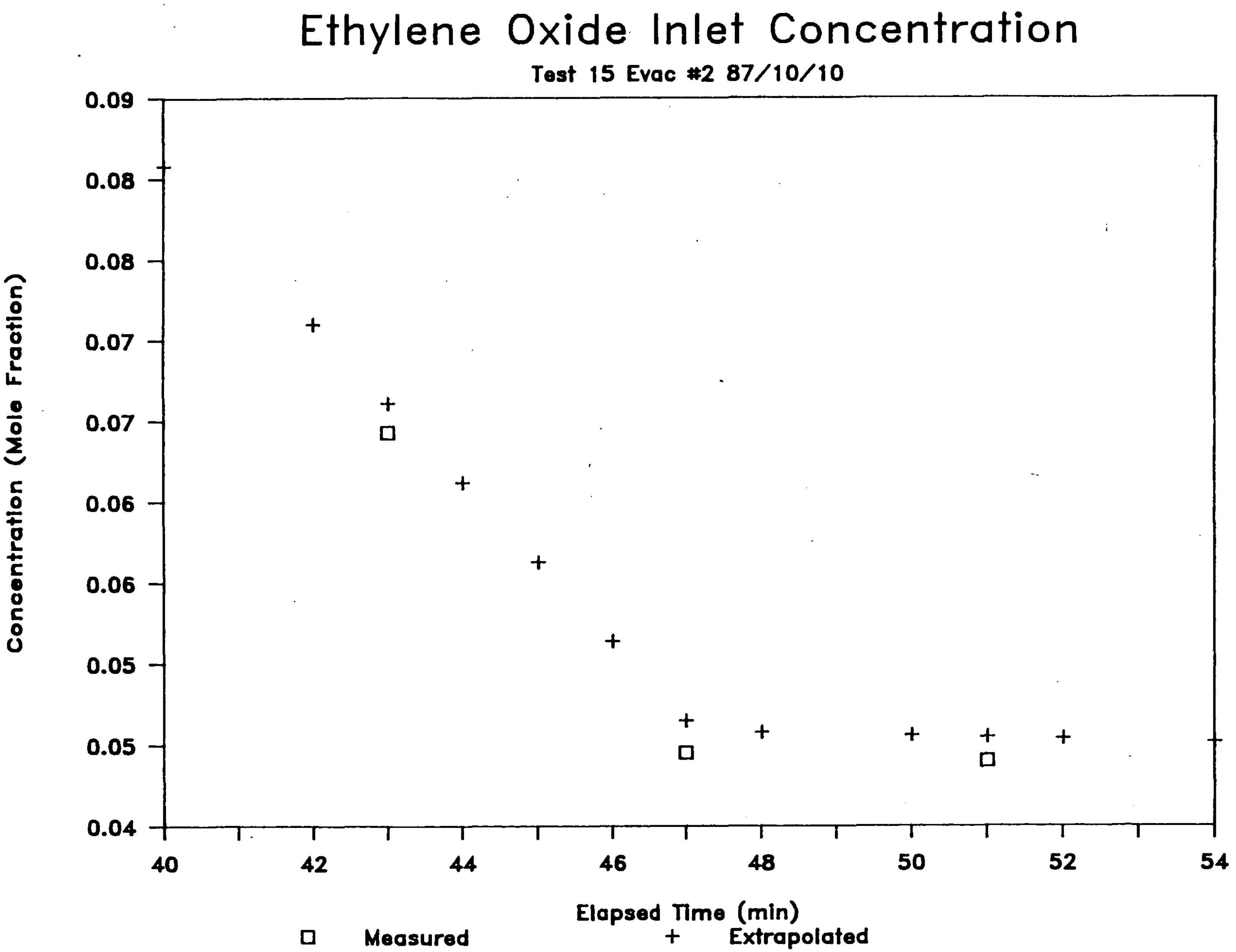

Figure 26. Interpolated EO Scrubber Inlet Concentrations for Test 15 Evacuation 1

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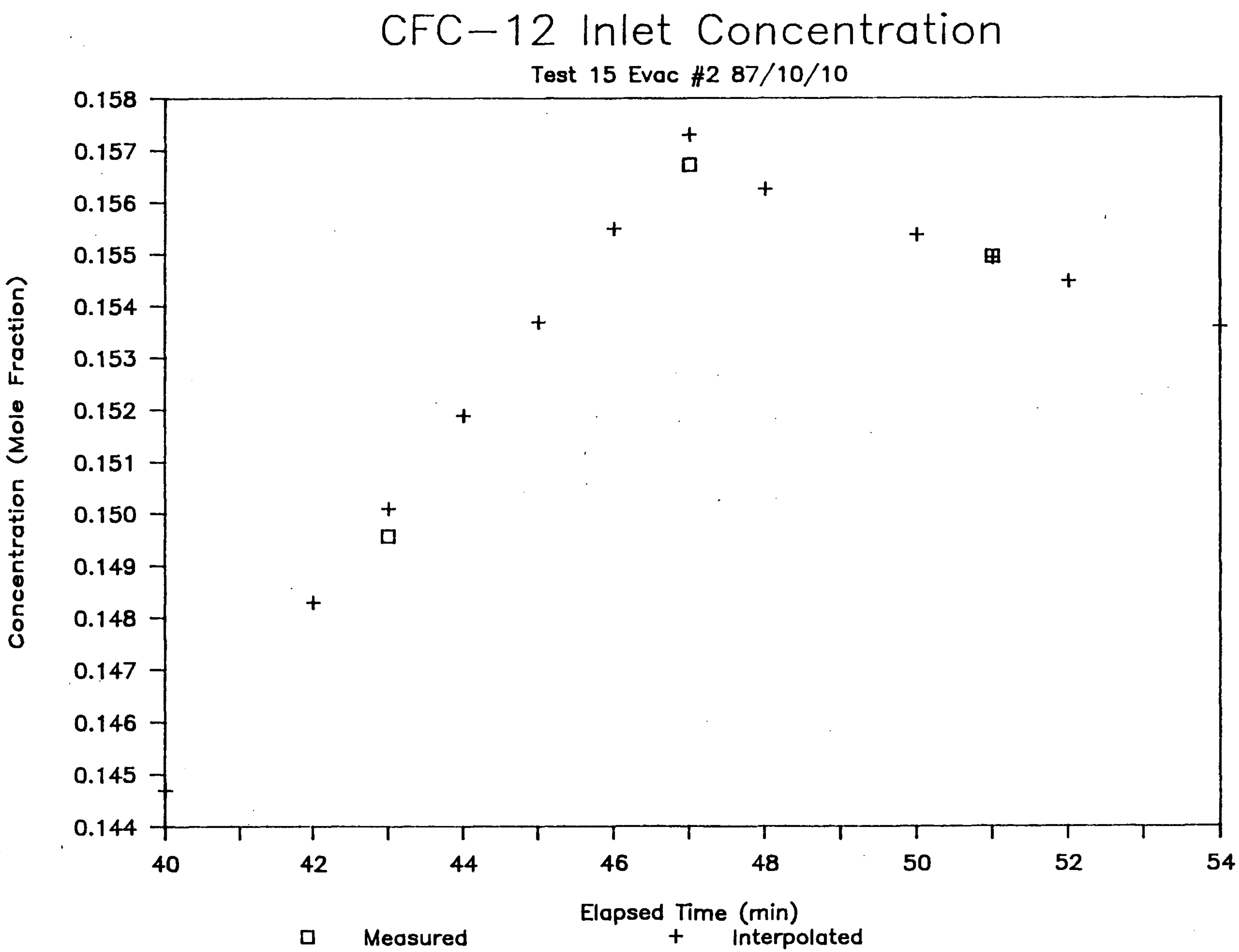

Figure 27. Interpolated CFC-12 Scrubber Inlet Concentrations for Test 15 Evacuation 2

The EO and CFC-12 concentrations were calculated as described above. The oxygen concentration was measured using Fyrite. For the first evacuations the oxygen was assumed to decrease exponentially from 20% to 0% by volume as shown in Figure 28. In several cases for the second evacuations the oxygen was assumed to increase as shown in Figure 29; however, in most cases either the average of all measurements was used or a value of 19% (v) was assumed. For the third through seventh evacuations the measured value was used or, if no measurements were taken, a value of 20% (v) was assumed.

Vent gas water content was measured using wet bulb/dry bulb measurements. Using the temperature differential and the dry bulb temperature, relative humidity was obtained from a table.[15] Another table was used to obtain the vapor pressure of water at the dry bulb temperature.[16] The mole fraction of water in the vent stream was calculated using Equation 1 presented in Section 4. The fraction of vent gas which was not attributed to EO, CFC-12, oxygen, or water was assumed to be nitrogen.

Ethylene Oxide Emission Rates

Both EO emission rates into and out of the control unit were calculated. The calculational procedures differed for the two locations because of the different procedures used to measure the flow rates.

Mass Flow Rate into the Control Unit--

The EO mass flow rate into the control unit was calculated based on the number of moles of gas exiting the chamber during each 2-min interval. Table 7 provides an example of the data used and the mass flow rates calculated during Test 6, Evacuation 1.

Assuming the chamber gas behaved as an ideal gas and using the chamber pressure (P, psia) and jacket temperature (T, K) provided on the chamber parameter printout sheet, the moles (mol) of gas leaving the chamber were given by:

$$\text{mol} = PV/RT \qquad \text{(Equation 10)}$$

where V was the chamber volume (1065 ft^3) and R was the gas constant (19.31 psia ft^3/[mol K]). Although the chamber gas probably deviated from ideal behavior, the assumption that it was ideal was a reasonable approximation at the chamber conditions used.

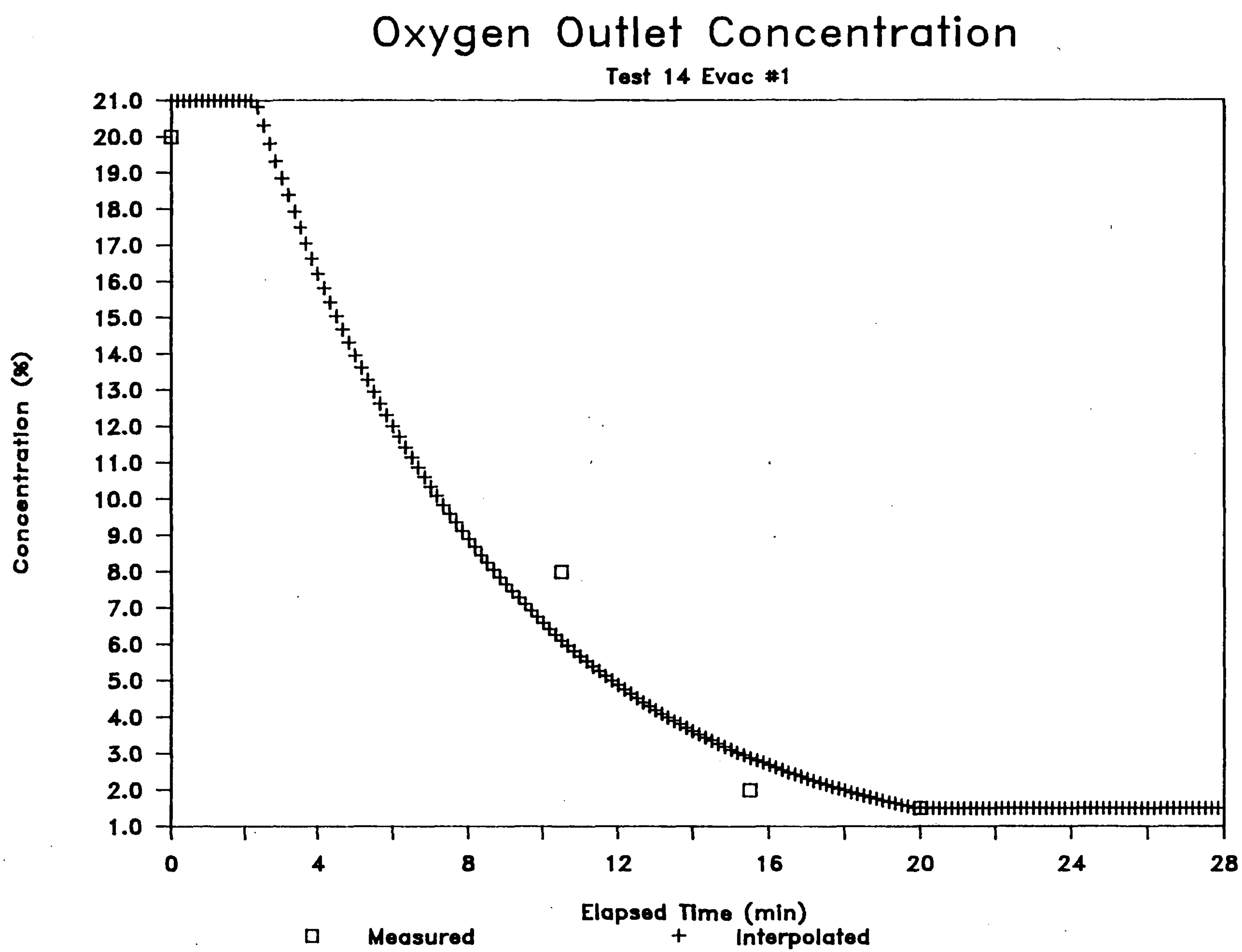

Figure 28. Interpolation of O_2 Scrubber Outlet Concentrations for Test 14 Evacuation 1

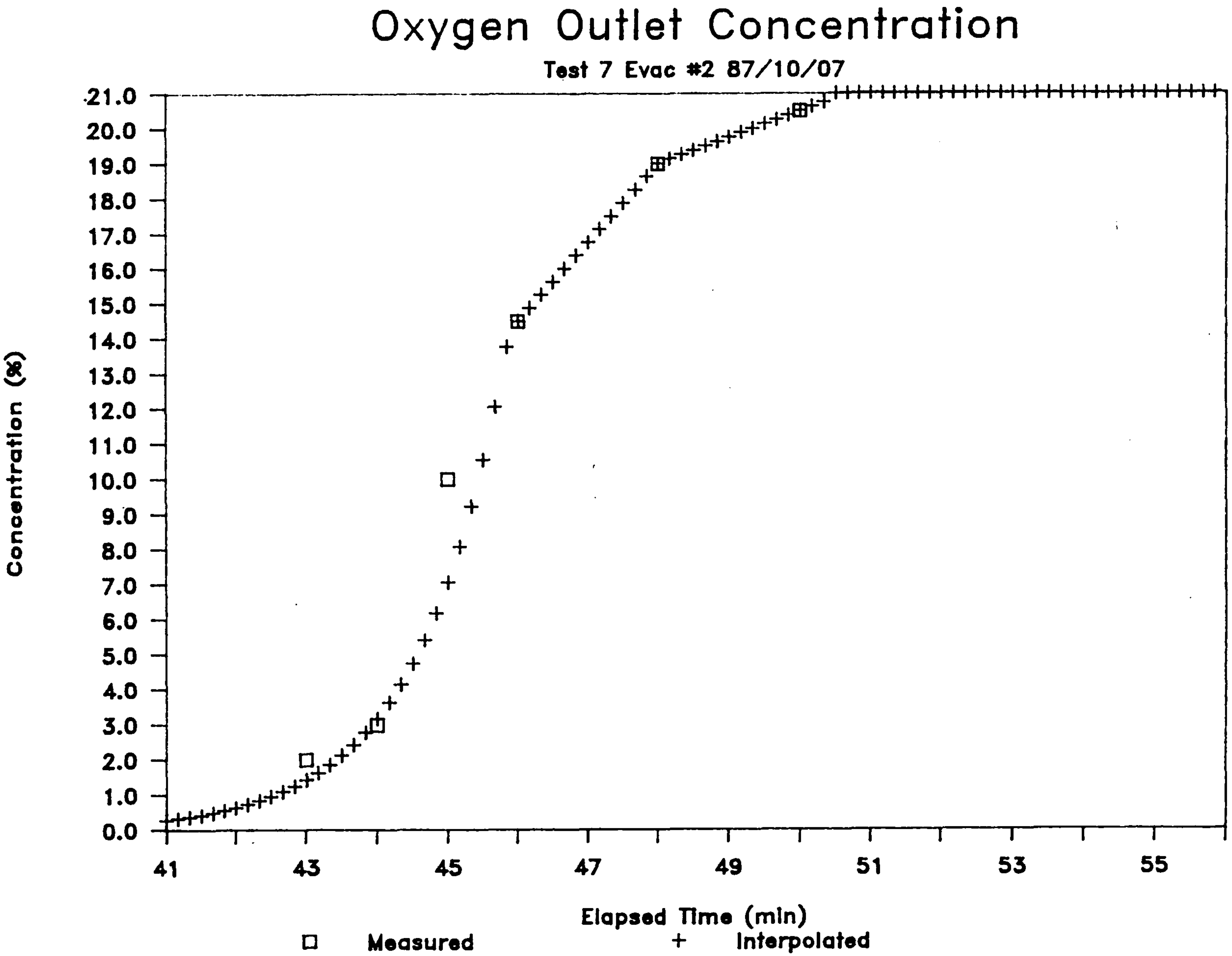

Figure 29. Interpolation of O_2 Scrubber Outlet Concentrations for Test 7 Evacuation 2

TABLE 7. ETHYLENE OXIDE MASS FLOW RATE INTO SCRUBBER DURING TEST 6, EVACUATION 1

Elapsed Time (min)	Clock Time	EO Conc. (% [v])	Molecular Weight (lb/mole)	Chamber Temp. (deg. C)	Chamber Pressure (psia)	Flow Rate (lb mol/min)	EtO Emission (lb/min)
2.00	21:41	19.79	83.03	53.1	21.4	0.18	1.57
4.00	21:43	20.43	84.04	52.2	19.2	0.18	1.63
6.00	21:45	21.07	85.56	52.7	17.2	0.17	1.59
8.00	21:47	21.71	87.16	52.7	15.6	0.14	1.29
10.00	21:49	22.35	87.22	52.6	13.5	0.18	1.74
12.00	21:51	22.99	87.29	52.0	11.3	0.18	1.87
14.00	21:53	23.63	87.36	51.9	9.5	0.15	1.58
16.00	21:55	24.26	87.45	51.9	7.5	0.17	1.81
18.00	21:57	24.90	85.66	51.8	5.6	0.16	1.76
20.00	21:59	25.54	83.87	51.5	4.2	0.12	1.33
22.00	22:01	26.18	82.08	51.3	3.3	0.08	0.88
24.00	22:03	26.82	80.30	51.1	2.6	0.06	0.70
26.00	22:05	27.46	78.51	51.6	2.2	0.03	0.41
						total lbs =	36.37

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The EO mass flow rate (R_{in}, lb/min) for EO into the control unit was given by:

$$R_{in} = MW_b C_b mol/t \qquad \text{(Equation 11)}$$

where MW_b was the molecular weight of EO (44 lb mol), C_b was the mole fraction of EO in the gas, and t was the time interval (2 min). The total weight (W_{in}, lbs) of EO entering the control unit was then given by:

$$W_{in} = \Sigma R_{in} \times t \qquad \text{(Equation 12)}$$

Emission out of the Control Unit--

The EO emission out of the control unit was calculated based on the pounds of gas exiting the control unit during each 10-sec interval. The total weight (W_{out}, lbs) of EO leaving the control unit was then given by:

$$W_{out} = \Sigma m \times t \qquad \text{(Equation 13)}$$

where m was the mass flow rate in lb/min and t was the time interval (0.16 min).

To calculate the flow rate of EO from the pressure drop across standard orifices Equations 3 and 4 from Section 4 were used. A Houston Instrument Digitizer was used to convert the stripchart lines representing continuous pressure readings across the orifice plates into numerical values. A BASIC program was used to interpret the electronic signals from the digitizer and generate a LOTUS 1-2-3 print file of the data. These data were imported into LOTUS. LOTUS spreadsheets were made for the 10 test runs, the seven evacuation sequences, and the two plate sizes.

Input parameters required by the program are:

- Chart speed = 28.3 inches/hr (0.2 mm/s),
- Baseline = 0 inches H_2O (0 kg/m^2),
- Full scale = 10 inches H_2O (254 kg/m^2),
- Standards = 2,
- Start time = varies according to test times, and
- Time intervals = 10 sec (interval between data readings).

The values for the input parameters were based on information from the stripcharts. Values listed above were used for each test run and both large and small orifice plates.

The mass rate of EO flow out of the control unit was then given by Equation 5 in Section 4.

Efficiency Calculations

Efficiency was calculated in terms of a throughput efficiency and a recovery efficiency.

Throughput Efficiency--

A throughput efficiency was calculated using the emissions into and out of the control unit. The throughput efficiency (E_T) is given by Equation 14.

$$E_T = 100 \times (W_{in}-W_{out})/W_{in} \qquad \text{(Equation 14)}$$

Recovery Efficiency--

A recovery efficiency was calculated using the weight of the original EO charge and the measured EO emissions at the outlet of the control unit. The weight of EO originally charged to the chamber was obtained by multiplying the weight of 12/88 gas by 0.12. No analysis was performed on the sterilant gas to verify the EO concentration. A correction was made for the EO remaining in the chamber (W_R) which was determined by Equation 15.

$$W_R = (MW_b C_b PV)/(RT) \qquad \text{(Equation 15)}$$

The mole fraction of EO left in the chamber was obtained from samples taken after Evacuation 7 either before or after the chamber had been refilled. The recovery efficiency (E_R) is then given by:

$$E_R = 100 \times (W_c-W_R-W_{out})/(W_c-W_R) \qquad \text{(Equation 16)}$$

where W_c is the weight of EO originally charged to the chamber.

RESULTS

The sampling and analytical method for EO emissions from sterilizers ultimately must be capable of determining whether a sterilizer EO control unit is operating efficiently. To do that the method must be capable of measuring the EO emissions accurately enough to provide consistent efficiency measurements. The sampling method must deliver unbiased sample and the analytical method must accurately identify and quantitate the components of interest.

In addition the test data was used to compare several options which exist in defining the method. A comparison was made between calculating efficiency by the Throughput Method and the Recovery Method and by using a chamber with product and without. The utility of the orifice plates was evaluated by comparing emission and efficiency results obtained using the orifice plates to results which would have been obtained if the flow rate had been estimated using the data from the chamber control monitor.

Sampling Method Evaluation

The sampling method was evaluated using a gas cylinder containing known concentrations of EO and CFC-12. The gas cylinder was first analyzed on the GC. Then the gas cylinder was treated as a sample by installing a tee between the cylinder and the sampling line. The flow rate of the gas out of the cylinder was adjusted so that there was always excess flow past the tee during sampling. Response of the cylinder sample through the sample line was compared to the response of the cylinder sample analyzed directly.

Evaluation of Inlet Sampling--

The inlet sampling bias was measured twice using a 2,508 ppmv EO and 6,022 ppmv CFC-12 standard. The total sampling and analytical bias in the EO measurement ranged from 0-7% with an average of 3.5%. The sampling bias in the EO measurement ranged from 0.2 to 11.9% with an average of 6%. In both cases the sampling was biased positively for EO indicating that the method would tend to overestimate EO emissions.

The total sampling and analytical bias in the CFC-12 measurement ranged from 4.3 to 12.5% with an average of 8.4%. The sampling bias in the CFC-12 measurement ranged from 0 to 15.2% with an average of 7.6%.

Evaluation of Outlet Sampling--

The outlet sampling bias was measured three times using a 502.4 ppmv EO and 1,200 ppmv CFC-12 standard. The total sampling and analytical bias in the EO measurement ranged from 1.9 to 12.9% with an average of 7.4%. The sampling bias in the EO measurement ranged from -7.5 to 7.1% with an average of +1.3%.

The total sampling and analytical bias in the CFC-12 measurement ranged from -9.5 to 4.8% with an average of -2.4%. The sampling bias in the CFC-12 measurement averaged 11%.

Analytical Method Evaluation

The analytical method was evaluated using a gas cylinder containing concentrations of EO and CFC-12 that were certified to ±2 percent. The gas cylinder was analyzed on the GC using the same procedure as for the standard cylinders. Using the response of the cylinder sample and the prepared calibration curve, a measured concentration of the cylinder sample was calculated. The measured concentration was compared to the expected or known concentration of the gas cylinder.

Evaluation of Inlet Analysis--

The inlet analysis bias was measured twice using a 2508 ppmv EO and 6022 ppmv CFC-12 standard. The analytical bias in the EO measurement ranged from -0.2 to -4.4% with an average of -2.3%. In both cases the analytical bias was negative. The analytical bias in the CFC-12 measurement ranged from -2.4% to 4.3% with an average of 1%.

Evaluation of Outlet Analysis--

The outlet analysis bias was measured three times using a 502.4 ppmv EO and 1200 ppmv CFC-12 standard. The analytical bias in the EO measurement ranged from 0.3 to 10.1% with an average of 6.2 percent. In all cases the analytical bias in the EO measurement was positive.

The analytical bias in the CFC-12 measurement ranged from -5.6 to -18.5% with an average of -12 percent. In all cases the analytical bias in the CFC-12 measurement was negative, indicating that the column may be overload by the combination of the 2-mL sample size and the high CFC-12 concentration.

Method Utility in Emissions Determination

The utility of the method in determining emissions was evaluated by comparing the measured EO emissions for the six empty chamber tests on the assumption that the control device efficiency did not change with time. Emissions data are presented in Table 8.

Emissions from Uncontrolled Sterilizers--

The expected quantity of EO entering the control unit during the six empty chamber tests ranged from 41 to 44 lb and averaged 42 lb. These values were based on 12% of the total weight of the 12/88 charge. The measured quantity of EO entering the control unit during these same six tests ranged from 24 to 62 lb and averaged 47 lb. In Test 7 where the measured mass of EO entering the scrubber was low, the inlet sampling pump leaked during the first 10 minutes of the evacuation and the FID flame was extinguished during portions of the third and fourth evacuations. Test 9 and 10 were performed on a day when the EO standard calibration curve for inlet samples was lower than on other test days.

TABLE 8. CONTROL UNIT INLET AND OUTLET EO MASS FLOW RATE FOR THE EMPTY CHAMBER TESTS

Test Number	Initial EO Charged to Chamber (lb)	EO Left in Chamber ~~(10^3 lb)~~	EO Entering Control Unit Measured (lb)	EO Exiting Control Unit Measured (lb)
7	43.8	0.42 $\times 10^{-3}$	24.19[a]	0.043
9	41.5	1.5	60.59[b]	0.011
10	42.4	0.22	62.12[b]	0.029
12	41.5	0.16	44.00	0.011
14	42.0	0.16	48.80	0.021
15	41.2	0.07	52.82	0.014

[a]During Test 7 there was a leak in the inlet sampling pump during the first 10 minutes of the evacuation and the FID flame was extinguished during portions of the third and fourth evacuations. Loss of these samples may explain the lower mass of EO entering the control unit during this test.

[b]The EO standard calibration curve for inlet samples on October 8, 1987 was lower than on the other test days. This would have raised the measured EO concentrations, and caused the EO mass flow into the control unit to be over estimated.

The absolute difference between measured emissions and expected emissions was >40% for three tests and was <10% for only one test. In five of the six tests the measured emissions were larger than the expected emissions.

Emissions from Controlled Sterilizers--

The measured quantity of EO emitted to the atmosphere from the control unit during the six empty chamber tests ranged from 0.011 to 0.043 lb and averaged 0.022 lb. The relative standard deviation (RSD) in these six measurements was twice the RSD for the inlet measurements indicating that more variation is associated with the scrubbing process than with the sterilization chamber.

Conclusions--

Most of the error in the EO mass flow rate and emission measurements probably resulted from errors in the interpolation of the flow rate/concentration profile. Ethylene oxide emissions were measured with greater precision at the scrubber inlet than at the scrubber outlet as was expected because of the higher concentrations at the inlet. Part of this loss of precision in EO emission measurement may be due to difficulty in identifying the EO peak in the chromatogram because of EO retention times that shifted as the EO concentration decreased.

<u>Method Utility in Control Unit Efficiency Determination</u>

The utility of the method in determining control unit efficiency was evaluated by comparing the measured throughput efficiencies obtained from the six empty chamber tests on the assumption that the control device efficiency did not change with time. All of the empty chamber tests were performed on the same chamber. Efficiency data for the empty chamber tests is presented in Table 9. The measured efficiency using the throughput method with the data from the six empty chamber tests ranged from 99.82 to 99.98% and averaged 99.94 percent. The median efficiency was 99.96 percent. Efficiency values were above 99.95% in five of the six tests. The one test in which the efficiency was below 99.9% was Test 7 where sampling and analytical problems were encountered as footnoted in Table 9.

TABLE 9. EFFICIENCY FROM EMPTY CHAMBER TESTS

Test Number	Throughput Efficiency	Recovery Efficiency
7[a]	99.82%	99.90%
9	99.98%	99.97%
10	99.95%	99.93%
12	99.98%	99.97%
14	99.96%	99.95%
15	99.97%	99.97%

[a]During Test 7 there was a leak in the inlet sampling pump during the first 10 minutes of the first evacuation and the FID flame was extinguished during portions of the third and fourth evacuations. The test was halted at these times until the problems were solved. This may explain the lower efficiencies measured during Test 7.

Effect of Calculational Method on Efficiency Determination

Comparisons of the groupings shown in Table 9 were done by a one-way analysis of variance (ANOVA) with sampling-calculational procedures as a fixed factor. The model was:

$$Y_{ijk} = \mu + M_i + e_{k(ij)} \qquad \text{(Equation 17)}$$

where

Y_{ijk} = the efficiency results,

μ = overall mean efficiency,

M_i = the calculational procedures, i=1 or 2, for Throughput and Recovery Procedures, respectively,

$e_{k(ij)}$ = the error term.

The M_i interaction term was tested to determine if there was a significant effect on efficiency results based on the calculational procedure used.

Basically, the error in the means of the efficiencies (the dependent variable) calculated using the Throughput and Recovery Methods are compared to the error in all the individual measurements using a F-Ratio. From the F-Ratio a probability (P) that the independent variable (the method used) has no effect can be calculated. If $P \leq 0.05$, then the effect is taken to be significant. If $P \leq 0.01$, then the effect is taken to be highly significant. A one-way ANOVA resulted in a P of 0.86 for the tests using chambers which did not contain product and 0.32 for the tests using chambers which did contain product; therefore, the procedure used to calculate the efficiency does not significantly affect the efficiency determined.

Effect of Product Presence on Efficiency Determination

The efficiency results from the tests where product was present in the chamber were compared with the efficiency results from the tests were product was not present in the chamber using a fixed factor ANOVA. The model was

$$Y_{ijk} = \mu + M_i + F_j + MF_{ij} + e_{k(ij)} \qquad \text{(Equation 18)}$$

where

Y_{ijk} = the efficiency results,

μ = the overall mean efficiency,

M_i = the procedure, i = 1 or 2, for Throughput or Recovery Procedure, respectively,

F_j = the chamber condition, j = 1 or 2, for chamber without and with product, respectively,

MF_{ij} = the MF_{ij} interaction term, and

$e_{k(ij)}$ = the error term.

A fixed factor ANOVA was used because the interaction terms, M_i and F_j, represented parameters that were fixed, i.e. the chamber either did or did not contain product. The M_i interaction term represented the effect of calculational procedure on the efficiency measurement. The F_j interaction term represented the effect of the presence of product on the efficiency measurement. The MF_{ij} interaction term represented the combined effect of the calculational procedure and the chamber condition on the efficiency measurement. The error term represented the random error of the method. The variances in calculating the efficiencies by the various methods were compared using an F-Ratio. From the F-Ratio, a probability that the independent variable does not effect the efficiency was calculated. If $P \leq 0.05$, then the effect is taken to be significant. The results of the ANOVA calculations are reported in Table 10.

None of the dependent variables tested had a $P \leq 0.05$. Therefore, there was no significant effect on the efficiency measurement due to the presence of product in the chamber. Furthermore, there was no interaction between the calculational method used and the presence or absence of product in the chamber. Thus, the efficiency results were within random error of the overall mean efficiency.

Orifice Plate Measurements Compared to Use of Monitor Data

Several outlet EO emissions were calculated using the chamber pressure and temperature data used to calculate inlet flow rates. Results are reported in Table 11. No correction was made for the change in the gas composition which occurred while the gas was in the scrubber. The largest change in gas composition occurs during the first evacuation when the gas composition changes from 30/70 % (v) EO/CFC-12 entering the scrubber to <1/>99 % (v) EO/CFC-12 exiting the scrubber. This meant that during the first evacuation approximately 30% of the moles of gas entering the control unit did not exit the control unit. Thus, the actual flow rate of the gas coming out of the control unit was probably less than the flow rate calculated by this method. This method should over-estimate EO emissions, resulting in an under-estimation of the control unit efficiency.

TABLE 10. FIXED FACTOR ANALYSIS OF VARIANCE RESULTS

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-Ratio	P
M_i	0.00048	1	0.00048	0.3034	0.59
F_j	0.00133	1	0.00133	0.8427	0.37
MF_{ij}	0.00012	1	0.00012	0.0758	0.79
$e_{k(ij)}$	0.02532	16	0.00158		

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TABLE 11. EMISSIONS AND EFFICIENCIES CALCULATED USING ESTIMATED FLOWS

Test Number	Weight EO Emitted (lb)	Throughput Efficiency	Recovery Efficiency
6	0.006	99.99%	99.99%
7	0.036	99.85%	99.92%
8	0.012	99.95%	99.98%
9	0.010	99.98%	99.98%
10	0.006	99.99%	99.99%
15	0.014	99.97%	99.97%

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Statistical comparisons of data in Table 11 with data in Tables 8 and 9 using a one-way ANOVA with flow-calculational procedures as a fixed factor showed that the EO emissions from the scrubber calculated using orifice plate data were not significantly different from the EO emissions estimated using chamber temperatures and pressures. The probability that there was no difference in the calculated EO emissions was 0.35; in the calculated throughput efficiencies, 0.59; and in the calculated recovery efficiencies, 0.25. A probability of 0.05 indicated a significant difference. The calculated efficiencies were not significantly different due to the high efficiency of the EO control unit. Therefore, in tests performed on units that are closed systems, flow estimation may be a possible alternative to orifice plate installation.

Vane Anemometer Data Compared to Orifice Plate Data

Several outlet EO emissions were calculated using the vane anemometer data. Results are reported in Table 12. The vane anemometer velocity readings were multiplied by the square root of the ratio of the molecular weight of air to the molecular weight of the vent gas stream. The corrected velocity readings were converted to volumetric flow rates by multiplying by the cross sectional area of the stack. The volumetric flow rates were corrected to standard conditions and converted to molar flow rates. Multiplying the molar flow rates by the vent gas molecular weight gave the mass flow rates. A correction was made for the time no flow was observed by multiplying the mass flow rate by 0.375. (Actual flow out of the stack occurs during only 37.5% of the total time required to evacuate the chamber.)

Comparison of data in Table 12 with data in Tables 8 and 9 show that the calculated EO emissions are much greater and the efficiencies lower using the vane anemometer data. This is because the vane anemometer data tends to overestimate the flow rate. Figure 15 shows the cyclical nature of the flow emitted from the scrubber. The vane anemometer was read at two minute intervals, providing a velocity reading based on the flow during the proceding 16-second interval. Thus, the vane anemometer provides grab samples of the flow rate versus the orifice plates which provide a continuous pressure differential readout. The quality of the vane anemometer data may be improved by taking more frequent velocity readings but could never surpass the quality of the orifice plate data due to the mechanics of the anemometer measurements.

TABLE 12. EMISSIONS AND EFFICIENCIES CALCULATED USING VANE ANEMOMETER DATA

Test Number	Weight EO Emitted (lb)	Throughput Efficiency	Recovery Efficiency
9	0.232	99.62%	99.44%
10	0.175	99.72%	99.59%
12	0.235	99.47%	99.43%

DISCUSSION

During the test several interesting problems arose and observations were made regarding the operation of the EO control device, the sterilization exhaust process, and the analytical system. These problems and observations will be discussed in this section as well as some possible modifications to the method.

Ethylene Oxide Control Device Operation

The system is designed so that the sterilization chambers can not exhaust until the control device is ready. At the end of the exposure cycle, the scrubber receives a signal from the sterilizer control panel that the chamber is ready to exhaust. The scrubber system starts up and requires a two-minute period before chamber evacuation can begin. During this two-minute period the gas from the previous chamber exhaust is emitted from the stack. At the end of the two-minute period, evacuation of the current chamber gas begins. An additional five to seven minutes is required before the chamber gas reaches equilibrium measured by the oxygen content taken during the 10 minutes of the first and second chamber exhausts.

Thus, during the first two minutes of the evacuation the concentrations of EO and CFC-12 should be the same as they were at the end of the previous exhaust and should be fairly constant. During the next five to seven minutes the EO and CFC-12 concentrations should change rapidly as the old chamber gas is swept out of the stack and the remaining chamber gas is diluted by the new chamber gas entering the scrubber. After 10 minutes the measured concentrations should level off to lower values than in the previous evacuation.

With this process cycle, a minimum of three samples would be required to characterize each evacuation, one during the first two minutes, one between two and seven minutes, and one after 10 minutes. The tested sampling/analytical method allows only three samples to be taken during each evacuation. With careful planning the exhaust could be sampled at one minute, five minutes, and 11 minutes. It is recommended that a minimum of six samples be taken. Two samples could be taken during each of the three predicted phases of the evacuation. This criterion would require either an analytical system capable of acquiring samples at 1-min intervals, a dual analytical system for each sampling port, or the collection of samples in a suitable container for later analysis.

Chamber Evacuation Process

The chamber is evacuated in pulses generated by a solenoid valve opening and closing to prevent the chamber from evacuating too rapidly. At the facility tested, the solenoid was open for 15 sec and closed for 25 sec. Operating with relay control, the gas flow out of the chamber and control unit is not continuous; however, the sampling system is a continuous process. The sampling system is composed of pumps which constantly are pulling sample out of the stack. Since, the chamber is not constantly exhausting, it could be possible for the sampling system to pull ambient air back through the stack, diluting the sample.

To maintain sample integrity, the sampling system must not pull more sample out of the stack than what is contained in the stack during the time period when the solenoid valve is closed. This can be accomplished by controlling the rate at which the sampling pumps pump and by increasing the size of the stack extension. The stack extension used for this test contained approximately 2.6 ft^3 and the main sample pump pulled a maximum of 10-15 L/min. So during the 25 sec period when the solenoid valve was closed, the pump pulled a maximum of 10 L of sample which is <10% of the stack extension volume. Thus, under the test conditions dilution of the sample when the solenoid valve was closed should not have occurred.

Analytical Method

The analytical method is deficient in several areas. Some are due to the characteristics of the vent gas and others to the characteristics of the analytical column.

Problems Due to Vent Gas Characteristics--

Three characteristics of the vent gas which pose problems for the on-line analysis of EO and CFC-12 are the relative concentrations of the EO and CFC-12, the high CFC-12 concentrations present in the first evacuation, and the presence of other interfering materials in the vent gas. The quantitation of CFC-12 is required for determining the molecular weight of the vent gas. The molecular weight is only needed if an orifice plate or a vane anemometer is used to measure the flow rate.

At the scrubber outlet, the EO is present at low ppmv levels and the CFC-12 is present at levels ranging anywhere from 500 ppmv to 99 volume percent. This wide difference in concentration makes the analysis of the two components on the same analytical column very difficult, but it can be done by programming the detector range. A sensitive range can be used for the EO and a less sensitive range for the CFC-12. To program the detector range successfully, near baseline separation of the two compounds must be obtained. Although this is possible with the analytical column chosen, baseline separation extends the time required for analysis and reduces the number of samples which can be collected and analyzed during an evacuation. Also, programming the detector range is further complicated when using the Fluorcol column due to the dependence of retention time on sample concentrations.

The high concentration of CFC-12 (90-99% [v]) in the first evacuation complicates the quantitation of the CFC-12 for two reasons, the calibration curve tends to be nonlinear over the entire concentration range and 99.9% (v) CFC-12 is necessary for the high point on the calibration curve. Accuracy of the CFC-12 quantitation may be improved by dilution of the sample. Sample dilution will introduce errors caused by sample handling and may be difficult, but not impossible, to do with on-line analysis. Alternately, the CFC-12 injected on the column could be reduced by using small sample loops (0.1 mL), but this would increase the difficulty of detecting the EO if both compounds were analyzed on the same analytical column.

The presence of other components in the vent gas creates two problems. First, components eluting near the EO peak may create confusion in correctly identifying and quantitating the EO peak. Second, components which elute after the EO and CFC-12 extend the analysis time and decrease the number of on-line samples that can be collected and analyzed during an evacuation. Although these compounds are present at low concentrations, they create analytical difficulties because of the low EO concentrations (ppmv) which must be measured.

Problems Due to the Analytical Column--

With the current analytical column the retention times of EO and CFC-12 shift with concentration. Increases in EO concentration decreases EO retention time. Interaction of EO with the column coating and packing seems to be minimal and totally dependent upon EO concentration at the temperature tested (100°C). A column temperature higher than the optimum phase temperature was necessary to maximimize the number of samples obtained during each evacuation; however, the increased sample throughput at the higher temperature compromised the efficiency of the column. The magnitude of the EO retention time shifts may be reduced by operating at lower column temperatures but the required analysis time would increase and the number of samples analyzed during an evacuation would decrease.

The CFC-12 retention time shift with increasing concentrations occurs at concentrations above 12 percent. Thus, the CFC-12 retention time shift is only a problem during the first two evacuations. The use of small loops (0.1 mL) or the dilution of the samples should eliminate this problem.

The time required for complete analysis of a vent sample limits the number of samples that can be analyzed. Over 3 min are needed to elute the major components of the vent gas. This limits the number of samples which can be analyzed during an evacuation to three. A minimum of six samples per evacuations is recommended.

Recommended Method Modifications

First, the field test data indicate that a minimum of six samples should be acquired from the scrubber outlet during each evacuation, two samples during the first 2 min, two samples between 2 and 9 min, and 2 samples after 10 min. This could best be accomplished off-line by taking grab samples in syringes or small gas sampling bags or cans and analyzing them later. However, this technique requires sample containers of the appropriate material of construction and proper storage procedures.

Second, the acquistion of off-line grab samples, allows the analysis to be performed under optimal conditions. That is, the column can be operated at lower temperatures, reducing the magnitude of the retention time shifts.

Third, the CFC-12 and EO should each be analyzed on a separate analytical system to optimize linearity. The CFC-12 should be analyzed on a system with a small gas sample loop (0.1 mL) and the EO on a system with a large loop (2 mL).

Conclusions

The sampling/analytical method adequately determined EO mass flow rate into and emissions out of the control unit; however, shifting EO retention times caused difficulty in measuring EO concentrations in the scrubber outlet emissions. Scrubber EO emissions based on orifice plate data gave similar efficiencies as efficiencies calculated from scrubber EO emissions estimated from chamber temperatures and pressures. The test data indicate that sampling at the control unit inlet and measuring control unit outlet flow rates with orifice plates, may not be necessary to obtain reasonable estimates of control unit efficiencies. Analytical bias of the method at the control unit outlet may be decreased by quantitating EO and CFC-12 on separate columns. Error in interpolation of the flow/concentration profile may be decreased by taking a minimum of six samples during each evacuation. Off-line sampling may improve both the quantitative ability of the analytical method and reduce the error in EO mass flow rate by optimizing analytical conditions and maximizing the number of samples that can be acquired. Also, the sampling/analytical method measured efficiencies precisely, and the efficiencies calculated were independent of the calculational procedure used, and the presence of product in the chamber.

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